

EPR for Catalysis Research

An international workshop on the application of EPR spectroscopy
in catalysis and on the role of electron spin in catalytic processes

Book of Abstracts

ORAL PRESENTATIONS

Surface Chemistry and Catalysis by EPR: Concepts, Examples and Perspectives.

Mario Chiesa

Department of Chemistry, University of Torino

mario.chiesa@unito.it

The interaction of a metal with a support is one of the primary factors affecting the catalytic activity of heterogeneous catalysts based on metals stabilized on inorganic supports under the form either of small particles or of single atoms or ions. The whole range of chemical bonding interactions are displayed at the metal/oxide interface, from weak dispersion forces to covalent bonds arising from the mixing of frontier orbitals. Understanding and tuning these interactions is key to tailor new catalysts, a notoriously difficult task in view of the complexity of polycrystalline surfaces. In this contribution, an overview of the wealth and breadth of information that can be obtained from EPR in the characterization of paramagnetic species in heterogeneous catalysts will be provided, illustrating the advantages that modern pulsed EPR methodologies can offer in monitoring the elementary processes occurring within the coordination sphere of surface transition-metal ions. Specific cases involving TMI acting as active catalytic sites will be presented, trying to outline the methodological approaches, which characterize the application of pulsed EPR techniques and the questions that can be answered and addressed relative to the characterization of heterogeneous catalytic materials.

EPR coupled to electronic structure methods for the characterization of active single-metal sites in microporous materials

Paolo Cleto Bruzzese¹, Sonia Chhabra,¹ Kavipriya Thangavel,² Andreas Poppl,² Alexander Schnegg¹

¹Max-Planck-Institut für Chemische Energiekonversion, 45470 Mülheim an der Ruhr, Germany

²Felix Bloch Institute for Solid State Physics, University of Leipzig, 04103 Leipzig, Germany

paolo-cleto.bruzzese@cec.mpg.de

The identification of the atomic architecture of the catalytically active sites occupies a central place in catalysis and it is the main prerequisite to determine mechanistic details of the catalytic reactions. Such knowledge is particularly important in microporous materials doped with transition metal ions where the attractive features of homogeneous and heterogeneous catalysts are combined.

Metal-Organic Frameworks (MOFs) represent a paradigmatic case of such systems. Indeed, their tunable structure enables to link the attractive features of homogeneous catalyst within the rigid porous framework promoting catalytic mechanism at the cross-road between homogeneous and heterogeneous catalysis.^[1] However, the complex and polycrystalline matrix prevents from a detailed understanding of the atomistic structure of the catalytically active sites and of their role in the reaction mechanism, especially when non-selective, bulk techniques are employed.^[2] On the other hand, spectroscopic techniques with single-site resolution enable correlation of spectroscopic features to specific metal centers limiting the interference from spectator sites. The rigorous spectroscopic finding can then be coupled to electronic structure calculations to associate a microscopic structure to the experimental spectrum and recover its structure-property relationship.^[3]

Here, Electron Paramagnetic Resonance (EPR) spectroscopy is used as site-selective technique to obtain exquisite insights on the geometric and electronic structure of paramagnetic active centers in MOFs as well as insights into their reaction mechanisms. Cutting-edge quantum chemical calculations of the EPR observables allow to establish correlation between the EPR parameters with electronic structure, directly linked to the reactivity of the open-shell species.^[4] Specific cases will be presented focusing on the interplay between EPR methodologies and sophisticated electronic structure methods.

References

- [1] X. Zhang et al. *Coord. Chem. Rev.* **2021**, 429, 213615.
- [2] B. E. R. Snyder et al. *Chem. Rev.* **2018**, 118, 2718–2768.
- [3] P.C. Bruzzese et al. *J. Am. Chem. Soc.* **2022**, 144(29), 13079–13081.
- [4] K. Thangavel, P.C. Bruzzese et al. *Phys. Chem. Chem. Phys.* **2023**

Applications of EPR spectroscopy in chemical industry, with a focus on catalytic materials, and benchtop instrumentation

Karsten Seidel and Derek Elam

Analytical and Material Sciences, BASF SE, Ludwigshafen, Germany

Electron Paramagnetic Resonance (EPR) spectroscopy is a powerful analytical technique for probing paramagnetic species. It is a versatile tool for investigating catalytic materials and can provide insights into structure-function relationships.

This presentation aims to showcase how we make use of EPR spectroscopy in the context of chemical industry, with a particular focus on heterogeneous catalysis.

We will provide examples from our own work, which involves X-band benchtop EPR, and examples from the work of others relating to large-scale catalytic processes.

As regarding our own lab, the focus is typically on (relative or absolute) quantification of paramagnetic species, and less on the identification of species or structure elucidation. Yet, even in this simple way, EPR can give valuable insight that cannot simply be substituted by other methods. This said, we will also highlight synergies of the application of EPR in catalysis with other areas of expertise. In particular, we will show how well EPR and solid-state NMR spectroscopy complement each other, from the viewpoint of lab operations, and from a scientific point of view.

EPR Spectroscopy of Paramagnetic Complexes in Metal-Organic Frameworks

Andreas Pöppl

Universität Leipzig, Fakultät für Physik und Geowissenschaften, Linnéstr. 5, D-04103 Leipzig,

e-mail: poeppl@physik.uni-leipzig.de

Metal organic frameworks (MOFs) are a class of porous coordination polymers which exhibit interesting adsorptive, catalytic, and magnetic properties. This lecture will focus on two aspects of EPR spectroscopy in MOF materials with examples from our research, which are mainly related to host guest interactions.

One striking feature of some MOF materials is their flexibility of the framework and selective responsiveness to external stimuli such as gas adsorption leading to so called “breathing” and “gate pressure” effects. *In situ* EPR spectroscopy allows to explore such gas pressure dependent phase transformations of flexible MOFs. Otherwise, the presence of coordinatively unsaturated (CUS) metal ion sites is another interesting aspect of these porous materials leading to potential catalytic applications. Pulsed EPR offers the opportunity to investigate the interaction of small molecules in MOF materials with such CUS metal ion sites. The experiments may provide unique information about the specific adsorption site of the molecules, details about the geometry of the formed adsorption complex as well as the strength of the adsorption interaction.

Electronic Structure Analyses of Iron Complexes for Electrocatalytic Oxygen Reduction

Prof. Dr. Vera Krewald

TU Darmstadt, Department of Chemistry, Theoretical Chemistry

Alarich-Weiss-Str. 4, 64287 Darmstadt, Germany; vera.krewald@tu-darmstadt.de

Catalysts for the efficient activation and transformation of small molecules are essential stepping stones towards a future society that is independent of fossil resources. Fuel cells, for instance for automotive applications, rely on the oxygen reduction reaction. While cost-intensive platinum-based catalysts are considered state-of-the-art, single-atom catalysts (SACs) have shown competitive activity albeit at lower stabilities. SACs are prepared by pyrolysis of earth-abundant precursors and rendered as amorphous powders, which significantly hampers the precise identification of active sites and hence a strategic optimisation of activity and stability.¹

For Fe-SACs, the active sites are considered as single iron ions ligated by four nitrogen donors embedded in a graphene-like environment. Open questions concern the number and nature of axial ligands and the presence of dopants. This talk will illustrate how quantum chemistry and theoretical spectroscopy can aid in unravelling the identity of active sites. The influence of ligand field strengths on spectroscopic properties will be discussed for complexes with pyridinic and pyrrolic nitrogen donors, including the first iron complex with a pyridinic, conjugated, square-pyramidal coordination sphere.²⁻⁴ The implications for the discernibility of such active sites in *in situ* and *operando* experiments will be discussed.⁵⁻⁷

References

- 1 S. Wagner, H. Auerbach, C. E. Tait, I. Martinaiou, S. C. N. Kumar, C. Kubel, I. Sergeev, H. C. Wille, J. Behrends, J. A. Wolny, V. Schunemann, U. I. Kramm, *Angew. Chem. Int. Ed.* **2019**, *58*, 10486.
- 2 C. Gallenkamp, U. I. Kramm, J. Proppe, V. Krewald, *Int. J. Quantum Chem.* **2021**, *121*, e2639.
- 3 T. Marshall-Roth, N. J. Libretto, A. T. Wrobel, K. J. Anderton, M. L. Pegis, N. D. Ricke, T. Van Voorhis, J. T. Miller, Y. Surendranath, *Nat. Commun.* **2020**, *11*, 5283.
- 4 C. Gallenkamp, U. I. Kramm, V. Krewald, *Chem. Commun.* **2021**, DOI: 10.1039/D0CC06237E.
- 5 L. Ni, C. Gallenkamp, S. Paul, M. Kübler, P. Theis, S. Chhabra, K. Hofmann, E. Bill, A. Schnegg, B. Albert, V. Krewald, U. I. Kramm, *Adv. Energy Sustain. Res.* **2021**, *2*, 2000064.
- 6 L. Ni, C. Gallenkamp, S. Wagner, E. Bill, V. Krewald, U. I. Kramm, *J. Am. Chem. Soc.* **2022**, *144*, 16827.
- 7 C. Gallenkamp, U. I. Kramm, V. Krewald, *in preparation*.

EPR as a Toolbox for the Characterization of Intermediates in Small Molecule Activation at Transition Metal Centers: Oxygen Activation at Biomimetic Dinuclear Sites and CO₂ Reduction by a Co Complex

Ayan Bera,^a Can-Jerome Spyra,^b Kaltum Abdiaziz,^c Alexander Schnegg,^{c,d} Franc Meyer,^b Kallol Ray,^a and Thomas Lohmiller^{a,d}

^aInstitute of Chemistry, Humboldt-Universität zu Berlin, Berlin, Germany

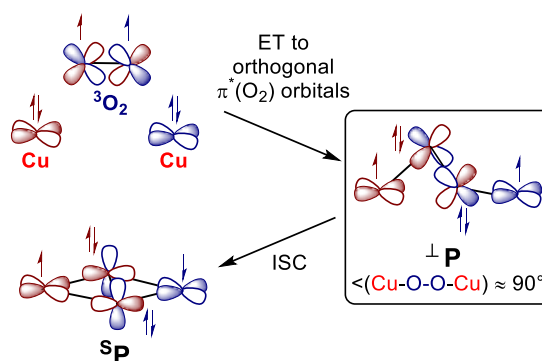
^bInstitute of Inorganic Chemistry, University of Göttingen, Göttingen, Germany

^cMax Planck Institute for Chemical Energy Conversion, Mülheim a. d. Ruhr, Germany

^dHelmholtz Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany

Small molecules are key substrates in processes that are central for sustainable energy scenarios, such as the reductive conversion of CO₂ into fuels or the reduction of O₂ in fuel cells. A major challenge due to their relative stability is their binding and activation by efficient, stable catalysts, ideally based on cheap materials, such as abundant transition metals. Rational design of improved catalysts requires profound understanding of the structural and electronic aspects that facilitate these steps. EPR spectroscopy provides a versatile toolbox for obtaining essential information on the catalysts and reactive intermediate states.

Here, we present recent examples of the application of EPR to understand the functioning of novel catalysts and biomimetic model complexes for oxygen activation [1, 2] and CO₂ reduction. This includes a series of stable $\mu\text{-}\eta^1\text{:}\eta^1$ -peroxodicopper(II) intermediate models for the O₂ binding process in type III Cu proteins, for which the type and strength of the Cu^{II}-Cu^{II} spin exchange interaction plays a decisive role. Using frequency-domain THz-EPR, we developed a novel approach to directly probe magnetic transitions over a broad energy range up to several hundred cm⁻¹, including formally forbidden triplet-to-singlet transitions [1]. This allowed us to quantify the intricate spin couplings in detail and derive robust magneto-structural correlations. On this basis, we propose a functional role of antisymmetric (Dzyaloshinskii-Moriya) exchange to overcome the spin-forbiddenness of O₂ activation at dicopper sites.



Scheme 1. Mechanism for O₂ binding at type III dicopper sites.

Furthermore, we present a novel Co-based electrocatalyst that very selectively and efficiently reduces CO₂ to CO. Isolation and EPR-spectroscopic investigation of 1- and 2-electron-reduced forms of the complex indicate redox-non-innocence of the Hbbpya ligand, the functional relevance of which will be discussed.

[1] Lohmiller, T.; Spyra, C.-J.; Dechert, S.; Demeshko, S.; Bill, E.; Schnegg, A.; Meyer, F. *JACS Au* **2022**, 2, 1134-11443.

[2] Battistella, B.; Lohmiller, T.; Cula, B.; Hildebrandt, P.; Kuhlmann, U.; Dau, H.; Mebs, S.; Ray, K. *Angew. Chem. Int. Ed.* **2023**, 62, e202217076.

Electronic Structures and Reactivity of Iron(V)- Nitrido and -Oxo Complexes

Shengfa Ye,* Wang Chen, Qiyi Miao

[†]State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China

High-valent iron species has attracted much interest in bio-inorganic chemistry, because they play key roles in important biological as well as industrial processes. Oxo-iron species have been identified as a pivotal intermediate in the catalytic cycle of a range of O₂-activating heme and nonheme iron enzymes. Nitrido-iron complexes are proposed to implicate in biological N₂ fixation and the Haber-Bosch process. Herein we present a combined spectroscopic and computational study on the electronic structures and reactivity of [Fe^V(N)TPP] (**1**, TPP²⁻ = tetraphenyl porphyrinate) and [Fe^V(N)(cyclam-ac)]⁺ (**2**, cyclam-ac = cyclam-1-acetate. Experimentally, both complexes register similar EPR spectra with an exceedingly anisotropic *g* values (*g*_⊥ ~1.7 and *g*_{||} ~1). In-depth analyses reveal that **1** and **2** feature an *S* = ½ orbitally nearly doubly degenerate ground state, and that the large *g*-anisotropy observed is the characteristic spectroscopic feature of low spin tetragonal iron(V)-nitrido and -oxo complexes.^[1] Starting from the experimentally validated electronic structure, reactivity of a range of iron(V)-nitrido and -oxo complex, such as oxygenation,^[2] N-N coupling and C-H activation,^[3] is discussed.

References

- [1] Chang, H.-C.; Mondal, B.; Fang, H.; Neese, F.; Bill, E.; Ye, S. *J. Am. Chem. Soc.* **2019**, *141*, 2421–2434.
- [2] Chang, H.-C.; Lin, Y.-H.; Werlé, C.; Neese, F.; Lee, W.-Z.; Bill, E.; Ye, S. *Angew. Chem., Int. Ed.* **2019**, *58*, 17589–17593.
- [3] Mondal, B.; Neese, F.; Bill, E.; Ye, S. *J. Am. Chem. Soc.* **2018**, *140*, 9531–9544.

CW-EPR spectroscopy in heterogeneous photocatalysis

Dana Dvoranová, Kristína Czikhartová, Zuzana Dyrčíková

Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, Bratislava, SK-812 37, Slovak Republic, e-mail: dana.dvoranova@stuba.sk

Nowadays, reduction of consumption of natural resources and searching for alternatives leads to the development of technologies, products, and materials which are environmentally harmonious and sustainable. Heterogeneous photocatalysis, which can convert light energy into chemical energy, regards as one of the most promising strategies in this field. The oxidative degradation of various organic pollutants up to water and carbon dioxide upon photoexcitation lies in the effective charge transfer processes upon photoexcitation of photocatalysts initiating the generation of paramagnetic species and radical intermediates. The nature and quantity of these species are determined not only by the photocatalyst properties, but also by the physicochemical factors affecting light absorption by the photocatalyst, the quantity, and nature of adsorbed species, desorption of products, or the interface properties. From this perspective, the electron paramagnetic resonance (EPR) spectroscopy offers its dominance because it represents a sensitive spectroscopic method that allows the detection and characterization of paramagnetic centers in different semiconducting nanomaterials which are significant for their photocatalytic properties. The continuous wave (CW) EPR measurements in the solid state, especially at low temperatures, bring us unique insight into the geometric and electronic structure of the paramagnetic sites relevant within the (photo)catalytic processes. Due to the transient character of paramagnetic species, mostly reactive oxygen species, generated upon exposure of photocatalytic dispersed systems, we are often forced to apply the indirect techniques to observe their generation. Besides the spin trapping technique, the spin scavenging technique, oxidation of sterically hindered amines, and photoreduction are often applied. All these techniques possess the valuable tool for the detection and characterization of transient species and the proper choice of suitable experimental conditions is crucial for their successful application in heterogeneous semiconductor systems and can help us to gain a comprehensive picture of the photoinduced processes undergoing upon light exposure of the photocatalysts in suspensions. The lecture is oriented on a short overview of the application of direct and indirect CW-EPR spectroscopy applied in heterogeneous photocatalysis [1-4].

Acknowledgements: This study was financially supported by the Scientific Grant Agency of the Slovak Republic (VEGA Project 1/0064/21) and Slovak Research and Development Agency under the contract Nr. APVV-21-0039.

- [1] Z. Barbieriková, D. Dvoranová, V. Brezová, *Mat. Sci. Photocat.*, Elsevier, **2021**, Ch. 8, 125.
- [2] D. Dvoranová, Z. Barbieriková, V. Brezová, *Molecules*, **2014**, 19, 17279.
- [3] D. M. Tobaldi, D. Dvoranová, L. Lajaunie, et al., *Mater. Today Energy*, **2022**, 15, 100974.
- [4] D. Dvoranová, M. Mazúr, I. Papailias, et al., *Catalysts*, **2018**, 8, 47.

Active Site Structure Determination in Ti-based Catalysts

Daniel Klose

ETH Zurich, Department of Chemistry and Applied Biosciences, Vladimir-Prelog-Weg 1-5,
8093 Zurich, Switzerland

Email: Daniel.Klose@phys.chem.ethz.ch

Paramagnetic organometallic catalysts, particularly based on the earth-abundant metals Fe, Cu and Ti, play an important role in providing novel roads to more sustainable chemical processes. In order to understand and optimize the catalytic processes, detailed structural information of the catalytically active metal sites in a heterogeneous environment is required. To determine the structures of paramagnetic metal sites, we use hyperfine sublevel correlation (HYSCORE) spectroscopy to determine electron-nuclear hyperfine couplings, particularly of ligand nuclei, and compare to predictions from DFT calculations that have been validated on organometallic model systems.[1,2,3]

Investigating a surface-supported Ti(III)-alkyl catalyst for olefin polymerization, we found that the hyperfine signature of Ti(III)-alkyl- ^1H nuclei are very sensitive to structural details and could be predicted well for molecular model complexes.[1] Extending the combined study by hyperfine spectroscopy and DFT modeling to a Ti(III)-nacnac complex grafted onto Al_2O_3 -700 by surface-organometallic chemistry showed that predictive quality of the DFT modelling is achieved also for nuclei beyond spin $S=1/2$, here namely ^{14}N (see Fig. 1). The low-temperature, low-pressure olefin polymerization activity of the Ti(III)-nacnac complex allowed us to conclude that ethylene insertion into the Ti(III)-alkyl bond proceeds via the augmented Cossee-Arlman mechanism.[2] Applying this methodology to Ziegler-Natta catalysts, where we could tune the number of active sites by addition of BCl_3 , we identified bimetallic alkyl-Ti(III)-Al species as the active sites of ethylene binding and subsequent polymerization.[3]

These insights enable more detailed studies, including targeted Ti(III)-model complexes, to address the tunability and specific properties of different Ziegler-Natta catalysts.

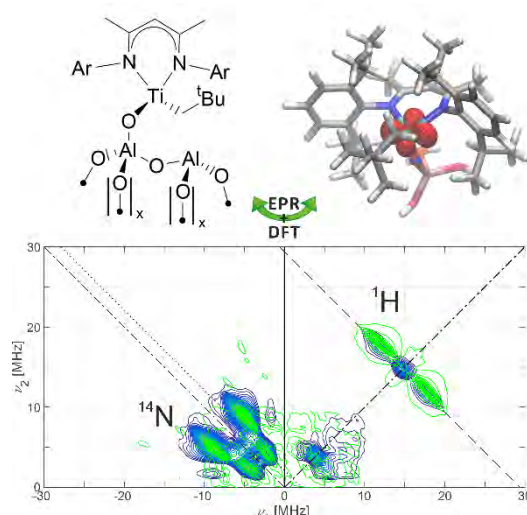


Figure 1. Ti(III)-nacnac@ Al_2O_3 . Chemical structure and spin density distribution (top) from comparison of HYSCORE (blue) and DFT prediction (green).

- [1] F. Allouche, D. Klose, C. Gordon, A. Ashuiev, M. Wörle, V. Kalendra, V. Mougél, C. Copéret, G. Jeschke, *Angew. Chem. Int. Ed.* **2018**, 57, 14533-14537.
- [2] A. Ashuiev, F. Allouche, N. Wili, K. Searles, D. Klose, C. Copéret, G. Jeschke, *Chem. Sci.* **2020**, 12, 780-792.
- [3] A. Ashuiev, M. Humbert, S. Norsic, J. Blahut, D. Gajan, K. Searles, D. Klose, A. Lesage, G. Pintacuda, J. Raynaud, V. Monteil, C. Copéret, G. Jeschke, *J. Am. Chem. Soc.* **2021**, 143, 9791-9797.

MAGNETIC RESONANCE (EPR/NMR) TO UNCOVER ELECTRONIC STRUCTURE OF SURFACE SPECIES IN HETEROGENEOUS CATALYSIS

Christophe Copéret

Department of Chemistry and Applied Biosciences – ETH Zürich, Switzerland

Heterogeneous catalysts are central to the chemical and polymer industry. These catalysts typically display multi-sites behaviors that have been associated with the ill-defined nature of these types of catalysts. Prominent examples are the Phillips and Ziegler-Natta catalysts based on Cr and Ti sites, respectively. Such complexity can be attributed to the multistep and multicomponent synthesis of these materials.

In this lecture, we will discuss how contemporary EPR and NMR spectroscopies combined with computational approaches can provide unprecedented information about the (electronic) structure of surface sites in these families of catalyst and enable to understand reactivity patterns at the molecule levels.

Deploying EPR and perturbation methods to study catalytic reactions

Prof. Damien Murphy

School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT

Opportunities and Limitations of In situ and Operando EPR Spectroscopy in Catalysis

Prof. Dr. Angelika Brückner, Leibniz-Institut für Katalyse
Albert-Einstein-Straße 29A, 18059 Rostock/D

EPR is a unique technique to detect paramagnetic species such as transition metal ions, trapped electrons, defects and radicals in solid and liquid catalysts. Usually this implies recording EPR spectra (in the case of operando EPR together with catalytic activity) well above ambient temperature and pressure. This is possible by implementing dedicated quartz reactors in the cavity of a cw-EPR spectrometer, in which catalysts can be heated, irradiated and/or exposed to electric fields, thus offering a lot of flexibility for following catalytic reactions [1].

In this presentation, the potential of EPR as an *in situ/operando* technique for analyzing structure-reactivity relationships in catalysis under reaction conditions is illustrated by two examples from homogeneous and heterogeneous catalysis.

Example I comprises homogeneous ethylene oligomerization catalyzed by a Cr complex (formed *in situ* from $\text{Cr}(\text{acac})_3$ and a $\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2$ ligand) in the presence of different AlR_3 activators. By applying *operando* EPR, supported by *in situ* UV-vis, ATR-IR, and XANES/EXAFS spectroscopy, the active Cr complex and the impact of the activator on the catalytic performance could be identified [2].

In Example II, *operando* EPR, *in situ* UV-vis, FTIR and XANES spectroscopy have been used to explore structure-reactivity relationships in $\text{V/Ce}_x\text{M}_{1-x}\text{O}_2$ catalysts ($\text{M} = \text{Zr, Ti, Mn, Fe}$) during low-temperature NH_3 -SCR of NO. Special $-\text{O}-\text{Ce}-\text{O}-\text{V}(=\text{O})-\text{O}-\text{M}-\text{O}-$ surface moieties have been identified in which redox shuttles of V, Ce and/or M ions are related to catalytic activity [3].

References:

- [1] S. A. Bonke, T. Risse, A. Schnegg, A. Brückner, Nature Rev. Methods Primers, **2021**, 1, Article No. 33 (<https://doi.org/10.1038/s43586-021-00031-4>).
- [2] R. Grauke, R. Schepper, J. Rabeah, R. Schoch, U. Bentrup, M. Bauer, A. Brückner *ChemCatChem* **12** (2020) 1025.
- [3] S. Keller, U. Bentrup, J. Rabeah, A. Brückner *J. Catal.* **408** (2022) 453.

Magnetic Resonance Characterization of spin effects at electrodes

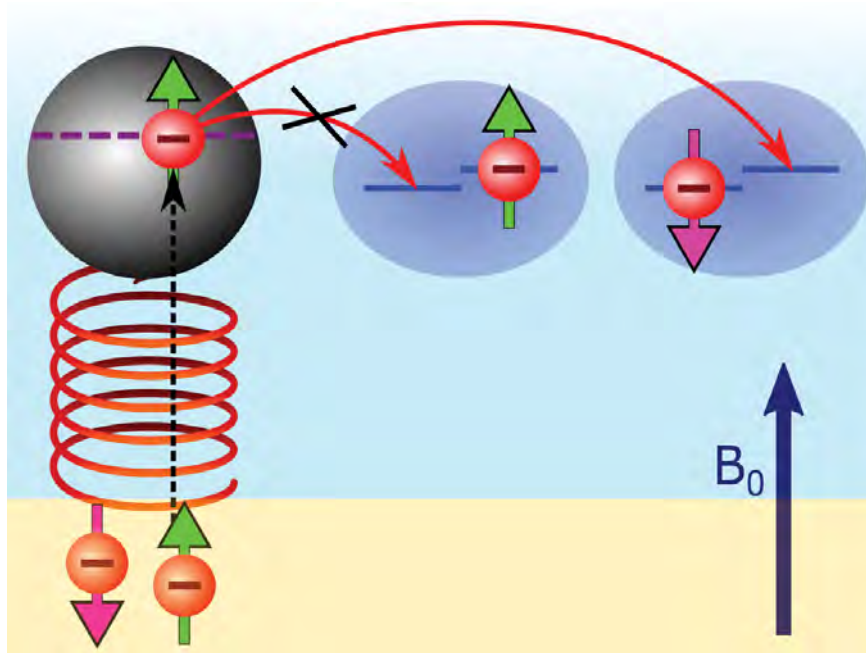
Prof. J-Ph. Ansermet, École Polytechnique Fédérale de Lausanne,
Institute of Physics, CH-1015 Lausanne-EPFL

Abstract

The author will first review quickly his involvement for about 10 years in probing the effect of conduction electron spin polarization on the NMR of molecules chemisorbed on catalysts (with Prof. C.P. Slichter) and electrodes (with Prof. A. Wieckowski) under potentiostatic control[1]. Then, electrically-detected magnetic resonance will be discussed in the framework of spintronics study of organic light emitting diodes (OLEDs) presenting organic magnetoresistance (OMAR)[2].

The main topic of the talk will be the characterization of “chirality-induced spin selectivity” of electrodes functionalized with polypeptides and helicene. The electrodes were either gold or GaAs pumped with circularly polarized light. Spin-dependent charge transfer were detected using EPR and electrochemical impedance spectroscopy [3].

Finally, a home-made 263 GHz EPR spectrometer will be presented, which admits as samples thin films of about 5mm in diameter [4], the size of a typical electrode.



[1] Phys. Rev. Lett. 1999, 83(12), 2457

[2] Phys. Rev. B 2014, 90, 201201(R)

[3] Phys. Chem. Chem. Phys. 2020, 22, 997

[4] APL Photonics 2016, 1(2), 026101

***In situ* and *operando* film-electrochemical EPR as a new tool to investigate 'heterogenised' molecular electrocatalysis**

M. M. Roessler

^aImperial College London, Molecular Sciences Research Hub, London W12 0BZ,
m.roessler@imperial.ac.uk

Unpaired electrons play an important role in a wide range of redox-driven catalytic processes in both chemistry¹ and biology². Controlling their location and exploiting the interactions with their environment can provide key mechanistic information into these catalytic reactions. In this talk I will discuss how we have used and developed EPR-based techniques to gain mechanistic insights into electrocatalysis.

I will introduce film-electrochemical EPR spectroscopy (FE-EPR) and show that it is a powerful tool to investigate surface-bound molecular catalysts, which are increasingly of interest in sustainable chemistry. With FE-EPR we have direct and accurate control over the redox state, even of 'buried' redox centres in proteins.³ We can further monitor the evolution of radicals during redox reactions, including catalysis, in real time under flow conditions, at room temperature and in aqueous solution.⁴ Such *in situ* and *operando* FE-EPR provides detailed insight into the mechanism of nitroxide-catalysed alcohol oxidation. FE-EPR gives access to substrate binding affinities, catalytic rate constants and reduction potentials during catalysis, and provides a new means of benchmarking electrocatalysts and their reactions. Lastly, I will provide an outlook for the application of FE-EPR to biocatalytic reactions.

- 1 M. M. Roessler and E. Salvadori, *Chem Soc Rev*, 2018, 47, 2534–2553.
- 2 K. H. Richardson, M. Seif-Eddine, A. Sills and M. M. Roessler, *Methods Enzymol*, 2022, **666**, 233–296.
- 3 K. Abdiaziz, E. Salvadori, K. P. Sokol, E. Reisner and M. M. Roessler, *Chemical Communications*, 2019, **55**, 8840–8843.
- 4 M. Seif-Eddine, K. Abdiaziz, S. Cobb, M. Bajada, E. Reisner and M. M. Roessler, *under review*.

A submersible EPR-on-a-chip dipstick sensor for applications in harsh environments

Authors: Silvio Künstner^{1,2}, Joseph E. McPeak^{1,3}, Anh Chu⁴, Belal Alnajjar⁴, Takuma Sato², Michal Kern⁴, Peter Fischer⁵, Klaus-Peter Dinse^{1,7}, Boris Naydenov¹, Alexander Schnegg², Jens Anders^{4,6}, Klaus Lips^{1,7}

¹Berlin Joint EPR Laboratory and EPR4Energy, Department Spins in Energy Conversion and Quantum Information Science (ASPIN), Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany

²EPR4Energy, Max-Planck-Institut für Chemische Energiekonversion, Mülheim an der Ruhr, Germany

³Novo Nordisk Foundation EPR Center, Department of Chemistry, University of Copenhagen, Copenhagen, Denmark

⁴Institute of Smart Sensors, Universität Stuttgart, Stuttgart, Germany

⁵Fraunhofer-Institut für Chemische Technologie, Pfinztal, Germany

⁶Center for Integrated Quantum Science and Technology (IQST), Stuttgart and Ulm, Germany

⁷Berlin Joint EPR Laboratory, Fachbereich Physik, Freie Universität Berlin, Berlin, Germany

Electron paramagnetic resonance (EPR) is the method of choice to investigate and quantify paramagnetic species in many applications in materials science, biology, and chemistry. In these fields, typical sample states include thin films [1] and solutions [2]. Of particular interest are dynamic processes in solution [3]. Their investigation, however, is limited by the form factor of the utilized microwave (MW) resonators as the entire process needs to be confined to the resonator [3]. The EPR-on-a-chip (EPRoC) dipstick device circumvents these limitations by integrating the entire EPR spectrometer into a single microchip, covered with a protective coating that enables the operation of the EPRoC submerged directly in the sample solution, thereby expanding the accessible sample environments for EPR measurements. In this approach, instead of a MW resonator, the coil of a voltage-controlled oscillator (VCO) with a size of a few hundred micrometers is simultaneously used as MW source and detector. As a test for the EPRoC dipstick and its protective coating, differently charged electrolyte solutions of a Vanadium redox flow battery with $\text{pH} < 1$ were investigated with the EPRoC and compared to conventional EPR results. The same linear relationship of EPRoC and EPR signal intensities with respect to the state of charge (SOC) was found, so that these experiments serve as proof-of-principle for a quantitative EPRoC dipstick device operating in a harsh sample environment.

Dipstick EPRoC with its inherent fast rapid scan (RS) capability using frequency sweeps allows the investigation of processes, in which time resolution is important. It has been shown recently [4] that the SNR per allocated acquisition time can significantly be enhanced, if measurement time for obtaining a full spectrum is the limiting factor, such as in oximetry and electrochemistry.

In combination with a permanent magnet, of which a first prototype will be presented, the EPRoC dipstick may find its way beyond the laboratory as a quantification tool for paramagnetic species in solution.

[1] M. Fehr et al., *Applied Physics Letters*, 101, 12, 12904, **2012**

[2] W. S. Chace et al., *Batteries*, 6, 4, 49, **2020**

[3] S. A. Bonke et al., *Nature Reviews Methods Primers*, 1, 1, 1-20, **2021**

[4] S. Künstner et al., *Magnetic Resonance*, 2, 2, 673-687, **2021**

Active centers in ATP-fueled motor proteins studied by combining solid-state NMR with EPR spectroscopy

Thomas Wiegand^{a,b}

thomas.wiegand@cec.mpg.de

^aMax Planck Institute for Chemical Energy Conversion, Mülheim/Ruhr (Germany)

^bInstitute for Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen (Germany)

In this contribution, I will discuss the potentials of combining solid-state NMR and EPR spectroscopy in characterizing catalytically-active sites using the example of ATP-driven motor proteins. DnaB helicases unwind double-stranded DNA by translocating along single-stranded DNA, a process which is powered by ATP-hydrolysis. Substituting the diamagnetic Mg^{2+} -cofactor with paramagnetic metal ions, such as Mn^{2+} and Co^{2+} , opens the way for paramagnetic NMR and EPR investigations.^[1] Paramagnetic relaxation enhancements (PREs) and pseudo-contact shifts (PCS) enable the positioning of the metal ion within the active pocket in case a low-resolution structural model is available.^[2] ELDOR-detected NMR spectroscopy identifies nuclei in the vicinity of the metal ion revealing structural insights in the transition state of ATP-hydrolysis trapped, for our spectroscopic studies, by using stable and non-hydrolysable ATP-mimics.^[3] Distance restraints between the ATP-analogue, DNA and the protein are for instance obtained from proton-detected fast magic-angle spinning experiments allowing for structural modelling of the ATP-binding pocket. I will also present approaches to site-specifically label the protein with cysteine-reactive maleimide tags carrying either a nitroxide radical or a lanthanide ion.^[4] Comparison of experimental PREs and model-predicted spin label-nucleus distances indicate that the size of the "blind sphere" around the paramagnetic center, in which solid-state NMR resonances are not detected, is slightly larger for Gd^{3+} than for nitroxide in ^{13}C -detected 2D spectra of DnaB.

References

- [1] T. Wiegand, D. Lacabanne, K. Keller, R. Cadalbert, L. Lecoq, M. Yulikov, L. Terradot, G. Jeschke, B. H. Meier, A. Böckmann, *Angew. Chem. Int. Ed.* **2017**, *56*, 3369-3373.
- [2] J. Zehnder, R. Cadalbert, L. Terradot, M. Ernst, A. Böckmann, P. Güntert, B. H. Meier, T. Wiegand, *Chem. Eur. J.* **2021**, *27*, 7745-7755.
- [3] A. A. Malär, N. Wili, L. A. Völker, M. I. Kozlova, R. Cadalbert, A. Däpp, M. E. Weber, J. Zehnder, G. Jeschke, H. Eckert, A. Böckmann, D. Klose, A. Y. Mulkidjanian, B. H. Meier, T. Wiegand, *Nat. Commun.* **2021**, *12*, 5293.
- [4] J. Zehnder, R. Cadalbert, M. Yulikov, G. Künze, T. Wiegand, *J. Magn. Reson.* **2021**, *332*, 107075.

Identification of active species and mechanisms in catalysis by operando EPR and reaction gas modulation

J. W. A. Fischer,¹ A. Brenig,² V. L. Sushkevich,² J. van Bokhoven,^{1,2} F. Buttignol,² D. Ferri,² G. Jeschke¹

¹ETH Zürich, Department for Chemistry and Applied Biosciences, Zürich, Switzerland

²Paul Scherrer Institute, Villigen, Switzerland

Industrial transition metal catalysts often contain several paramagnetic species, whereas not all of them may be active. Assignment of active species is most reliable if the catalyzed reaction proceeds in the EPR resonator and can be monitored by other techniques as well. Based on a home-built high-temperature continuous-wave (CW) EPR probehead with a water-cooled resonator, we have realized such an operando EPR setup that allows for controlled changes in the reaction gas stream by flow controllers and for on-line product analysis by mass spectroscopy. Due to the modular design, we can use the system as well for reactions that proceed in batch mode. We will demonstrate this on the example of oxidation of methane to methanol by a copper mordenite catalyst.

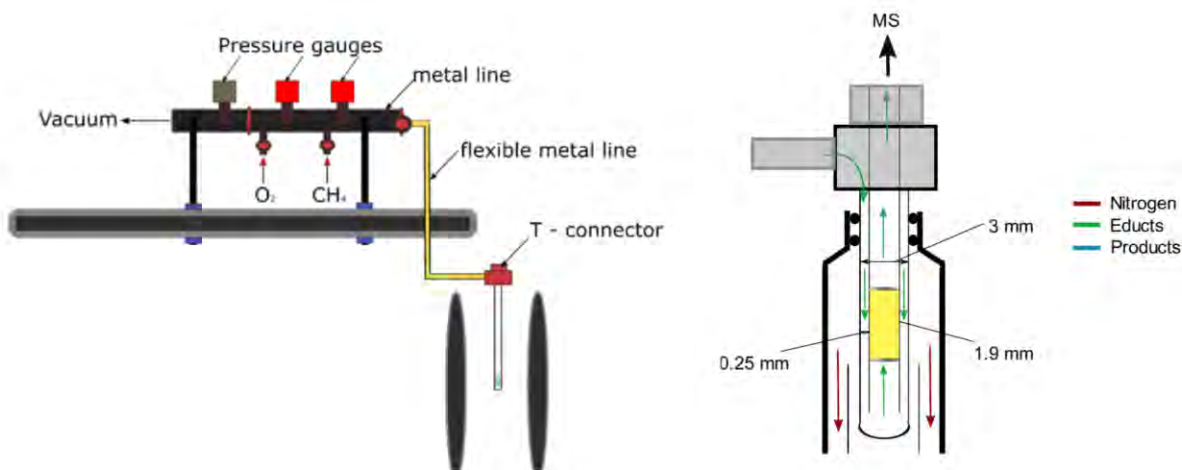


Figure: Operando EPR setup for methane oxidation to methanol by copper zeolite catalysts (left) and flow cell for use with a water-cooled high-temperature EPR resonator.

In many cases, EPR spectral changes of a heterogeneous catalyst occur on timescales of several minutes. For such systems, we can perform transient operando EPR with modulation excitation by acquiring individual CW EPR scans. We then compute phase-domain spectra by post-processing. A commercial Fe-exchanged ferrierite catalyst for simultaneous conversion of nitrous oxide and nitric oxide over will serve as an example for this approach.

While EPR spectroscopy is usually the most informative technique for paramagnetic species and can provide quantitative information, it is blind to diamagnetic species. Therefore, it is crucial to complement EPR spectroscopy by data from other techniques, as we will illustrate for both of our examples. In particular, we will discuss phase-resolved x-ray absorption near edge spectroscopy (XANES) data in conjunction with phase-resolved EPR spectra for the Fe-exchanged ferrierite catalyst.

Detection of paramagnetic intermediates in Nickel and Bismuth based organo-metallic catalytic systems

Dr. Edward Reijerse

Max-Planck-Institut für Chemische Energiekonversion, 45470 Mülheim an der Ruhr, Germany

Structure elucidation of a metalloDNAzyme

Müge Kasanmascheff / TU Dortmund

Over the last two and a half decades, DNAzymes have been demonstrated to catalyze various reactions, such as DNA cleavage, porphyrin metalation, and copper-mediated alkyne-azide 'click' cycloaddition, to name just a few.¹ Their potential applications include smart materials assembly, enantioselective synthesis, biosensing, and promising therapeutic reagents in cancer gene therapy.^{2,3}

As enantioselectivity and activity of metalloDNAzymes are determined by the ligand-bound structure and ligand environment, it is essential to gain an accurate structural understanding of the metalloDNAzymes for better catalyst design. In this talk, I will highlight our recent efforts to elucidate the structure and flexibility of a Cu²⁺-based metalloDNAzyme, which showed excellent yields (up to 99%) and enantioselectivity (up to 99% ee) for Michael addition.⁴

(1) Ma, L.; Liu, J. Catalytic Nucleic Acids: Biochemistry, Chemical Biology, Biosensors, and Nanotechnology. *Iscience* 2020, 23 (1), 100815. <https://doi.org/10.1016/j.isci.2019.100815>.

(2) Yum, J. H.; Park, S.; Sugiyama, H. G-Quadruplexes as Versatile Scaffolds for Catalysis. *Org. Biomol. Chem.* 2019, 17 (44), 9547–9561. <https://doi.org/10.1039/c9ob01876j>.

(3) Huo, W.; Li, X.; Wang, B.; Zhang, H.; Zhang, J.; Yang, X.; Jin, Y. Recent Advances of DNAzyme-Based Nanotherapeutic Platform in Cancer Gene Therapy. *Biophysics Reports* 2020, 6 (6), 256–265. <https://doi.org/10.1007/s41048-020-00123-w>.

(4) Punt, P. M.; Langenberg, M. D.; Altan, O.; Clever, G. H. Modular Design of G-Quadruplex MetalloDNAzymes for Catalytic C–C Bond Formations with Switchable Enantioselectivity. *Journal of the American Chemical Society* 2021, 143, 3555–3561. <https://doi.org/10.1021/jacs.0c13251>.

EPR insight into coordination and activation of small molecules – toward generation of reactive species on oxide and zeolite catalysts

Piotr Pietrzyk*, Kamila Sobańska, Bartosz Mozgawa, Zbigniew Sojka

Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, PL-30387 Krakow, Poland

e-mail: pietrzyk@chemia.uj.edu.pl

Spectroscopic magnetic techniques provide powerful and robust tools for gaining valuable information on chemical systems, including elusive reactive species often encountered in catalytic research. Those methods allow for study not only molecular systems but also extended structures of various geometrical aspects. With its inherent specificity and selectivity, electron paramagnetic resonance (EPR) spectroscopy is a versatile method for studying reactivity and dynamics of open-shell systems. From the perspective of catalysis and environmental chemistry, EPR provides quantification of paramagnetic species, their identification by means of spin-Hamiltonian parameters [1], and insight into interactions within the nearest neighborhood [2]. When radical reaction pathways are operating or open-shell systems are active centers, EPR spectroscopy is an invaluable tool to study their mechanisms [3].

Few examples of applications of EPR spectroscopy to procatalytic research will be discussed. They include (1) a study of non-Fenton oxides that are active in the generation of reactive oxygen species (ROS) through interaction with H_2O_2 [3], (2) role of surface oxygen species in advanced oxidation process (AOP) assisted by H_2O_2 [4], (3) the activation of dioxygen and nitric oxide by transition metal ions in zeolite channels [1,5]. The presented EPR results will be supported by other spectroscopic techniques such as IR, Raman, UV-vis, microscopic observations (TEM/STEM/EDS) and molecular modelling with density functional theory (DFT) methods.

Generation of reactive oxygen species through H_2O_2 decomposition is commonly catalyzed by transition-metal-based systems, but also less conventional materials of non-redox nature, such as amorphous oxides, exhibit specific activity in this process. The redox active materials show typical Fenton-like reactivity, while for the non-redox oxides formation of ROS is not trivial and involves interfacial electroprotic reactions [3]. Examples of discrete active sites (single cation active sites) will be discussed based on the transition-metal cations exchanged into zeolites (ZSM-5, CHA). They include zinc centers for binding and activation of dinitrogen, nickel for binding nitric oxide molecules and copper centers active in selective reduction of nitric oxide with ammonia.

Acknowledgment

This research was financially supported by the National Science Center, Poland (NCN), grant Sonata Bis7 2017/26/E/ST4/00794.

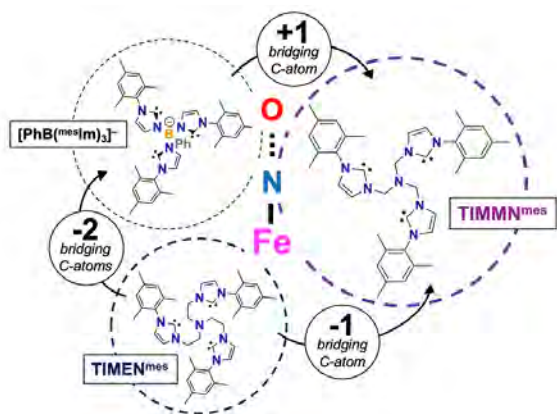
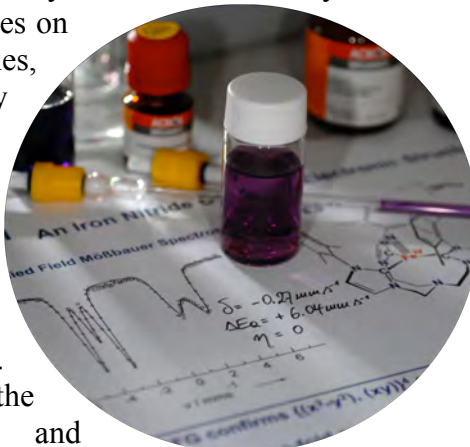
References

- [1] P. Pietrzyk, K. Góra-Marek, T. Mazur, B. Mozgawa, M. Radoń, M. Chiesa, Z. Zhao, Z. Sojka, J. Catal. 394 (2021) 206.
- [2] P. Pietrzyk, T. Mazur, K. Podolska-Serafin, M. Chiesa, Z. Sojka, J. Am. Chem. Soc. 135 (2013) 15467.
- [3] K. Sobańska P. Pietrzyk, Z. Sojka, ACS Catal. 7 (2017) 2935.
- [4] L. Wolski, K. Sobańska, M. Muńko, A. Czerniak, P. Pietrzyk, ACS Appl. Mater. Interfaces 14 (2022) 31824.
- [5] P. Pietrzyk, K. Podolska, T. Mazur, Z. Sojka, J. Am. Chem. Soc. 133 (2011) 19931.

“Super-Oxidized” Iron Nitrido & “Super-Reduced” Iron Nitrosyl Complexes in *tris*-Carbene Coordination Spheres – and How Iron Really Feels About it

Karsten Meyer | Friedrich-Alexander-University Erlangen – Nürnberg (FAU), Germany

Abstract: In this seminar, we will present our work on the synthesis and reactivity of metal nitrido and nitrosyl complexes. First, we report our studies on high-valent Fe(IV, V, VI and VII)^[1,2] nitrido complexes, synthesized *via* photolytic azide cleavage followed by oxidation with Ag^{II} and Xe^{II}-salts. In this series of complexes, the Fe≡N unit is stabilized by the sterically encumbered *N*-anchored *tris-N*-heterocyclic carbene chelates *tris*{2-(3-mesitylimidazol-2-ylidene)*alkyl*}amine (*alkyl*: methyl = TIMMN; ethyl = TIMEN). Based on the iron nitrido complex [(TIMEN^{Mes})Fe^{IV}(N)]⁺,^[1] we show how very subtle changes in ligand design (TIMEN vs. TIMMN) lead to tremendously different reactivity, and the stabilization and isolation of high-valent Fe(V)^[3] and super-oxidized Fe(VI)^[4] and highly reactive Fe(VII)^[4] complexes.



Subsequently, we address the question of to what extent the complexes' electronic and structural properties change when – formally – atomic oxygen is added to the nitrido ligand; thus, transforming a high-valent metal nitrido to a low-valent metal nitrosyl complex. Treatment of [(TIMEN^{Mes})Fe^{IV}(N)]⁺ with Me₃NO yields [(TIMEN^{Mes})Fe(NO)]⁺, thus providing access to a unique series of five iron nitrosyl complexes in a single ligand environment, [(TIMEN^{Mes})Fe(NO)]^m (*m* = 3+ to 1–), which – according to the Enemark & Feltham notation –

is formulated as {FeNO}^{6–10}. The synthetic study was complemented with in-depth crystallographic, spectroscopic, and computational analyses, giving detailed insights into the electronic structure of the currently most complete series of iron nitride and nitrosyl complexes.

Formally, the transformation of the all trigonal-symmetric Fe^{IV}≡N to {Fe–NO}⁶, or even {Fe–NO}⁹, is a two- or even five-electron reduction, respectively, which is expected to be associated with striking structural changes. However, the formally high-valent iron nitrides and low-valent iron nitrosyls are structurally remarkably similar; thus, questioning the concept of oxidation states in {Fe–N(O)}ⁿ complexes! At least in this series of complexes, we conclude that nitrosyls are better described as oxo-imidos, more related to the classic imido and nitrido complexes.^[5,6]

Key References

- [1] C. Vogel, F.W. Heinemann, J. Sutter, C. Anthon and K. Meyer in *Angew. Chem. Int. Ed.* **2008**, 47, 2681–2684.
- [2] J.J. Scepaniak, C. Vogel, F.W. Heinemann, K. Meyer and J.M. Smith in *Science*, **2011**, 331, 1049–1052.
- [3] M. Keilwerth, L. Grunwald, W. Mao, F.W. Heinemann, J. Sutter, E. Bill and K. Meyer in *J. Am. Chem. Soc.* **2021**, 143, 1458–1465.
- [4] M. Keilwerth *et al.*, to be submitted **2023**
- [5] M. Keilwerth, J. Hohenberger, F.W. Heinemann, J. Sutter, Scheurer, H. Fang, E. Bill, F. Neese, S. Ye and K. Meyer in *J. Am. Chem. Soc.* **2019**, 141, 17217–17235.
- [6] M. Keilwerth, W. Mao, S.V.A. Jannuzzi, L. Grunwald, F.W. Heinemann, A. Scheurer, J. Sutter, Scheurer, S. DeBeer, and K. Meyer in *J. Am. Chem. Soc.* **2023**, 145, 873–887.

Long-lived, ambient Cr(III)-based near-IR emission, and Donor-Acceptor Dyads for Upconversion Technologies

E. Richards*, S.J.A. Pope, N. Sawicka, J.M. Beames, A. Wright, Y-L. Wu

School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT
Email: RichardsE10@cardiff.ac.uk

Cr(III) complexes have attracted interest due to their optical,¹ (photo)redox and magnetic properties.² Cr(III) photoluminescence,³ from a discrete coordination complex was first reported in the 1960s.⁴ The photophysics of Cr(III) complexes is generally dominated by metal-centred excited states.^{5–7} A strong, pseudooctahedral ligand field at Cr(III) yields the possibility for populating doublet excited states (2 E and 2 T), while simultaneously preventing 4 T₂/ 2 E back intersystem crossing. As relaxation from these excited states to the 4 A₂ ground state is spin forbidden, long-lived phosphorescence can be observed. However, Cr(III) species are often hampered by poor emissivity. Herein, we report the development of luminescent Cr(III) complexes using 1,3-bis(20-pyridylimino)-isoindoline (bpi) derivatives as terdentate N⁴N⁴N ligands demonstrating long-lived near-IR emission.

We also introduce recent results using Time-Resolved EPR spectroscopy to investigate formation of triplet states in donor-acceptor chromophores, exploring the effects of spin-orbit coupling from heavy-atom on resulting electron transfer processes.

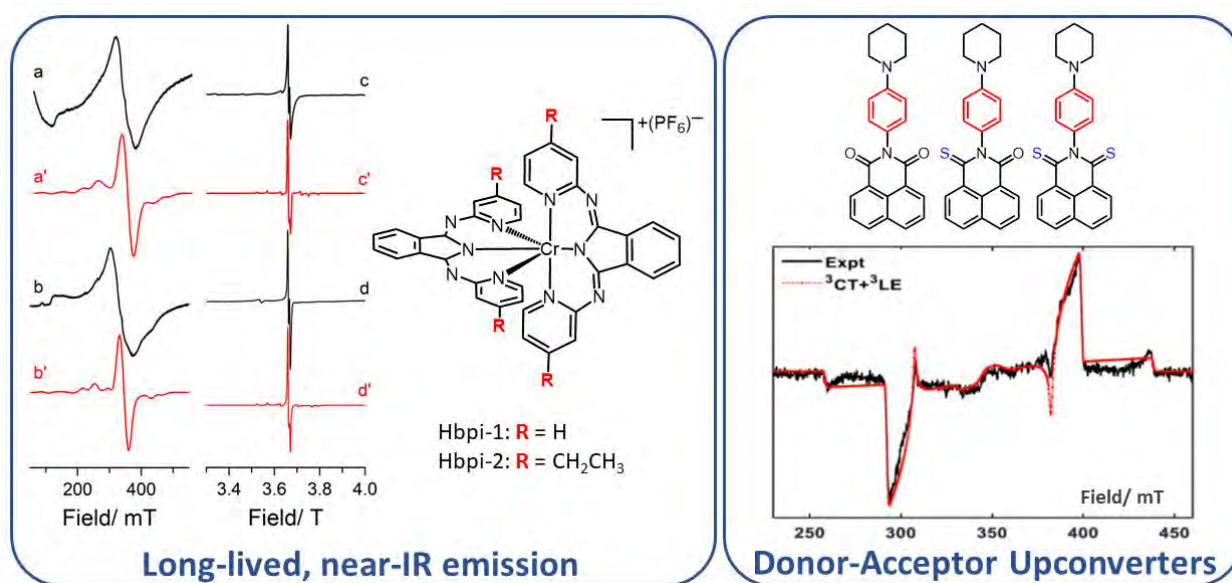


Figure. Multi-frequency and TR-EPR spectra on Cr(III) near-IR emitters and organic based donor-acceptor dyads for upconversion technologies

[1] Long-lived, near-IR emission from Cr(III) under ambient conditions, N. Sawicka, C. J. Craze, P. N. Horton, S. J. Coles, E. Richards, S. J. A. Pope, *Chem. Commun.*, **2022**, 58, 5733-5736

Bioinorganic redox modulation, catalysis and signaling for medical, environmental and energy applications

Ivana Ivanović-Burmazović

*Chair of Inorganic Chemistry - Bioinorganic Chemistry and Coordination Chemistry, LMU
Ivana.Ivanovic-Burmazovic@cup.uni-muenchen.de*

The talk will illustrate how investigations of redox reaction mechanisms (inner-sphere, proton or metal coupled electron transfer as efficient mechanism for chemical energy conversion) with involvement of metal complexes and some small inorganic entities, such as superoxide radical anion ($O_2^{\bullet-}$), nitrogen species (e.g., NO, nitrite), hydrogen sulfide (H_2S) and carbon dioxide (CO_2) can lead to new approaches for:

- i) modulation of oxidative stress, biological redox signaling, its (patho)physiological consequences and development of potential pharmaceuticals, adjuvants and therapy enhancers (for approaching longevity, cancer radiation therapy, neurovascular regulation of blood pressure and heart function, enhancement of covid-19 therapy and posttranslational redox modifications and
- ii) (electro)catalytic or stoichiometric transformations of small molecules of environmental and energy relevance.

Presented will also be applications of variety of physicochemical techniques (e.g., cryo-MS, cryo-stopped-flow, high-pressure stopped-flow, high-pressure NMR and high-pressure electrochemistry, as well as EPR) for thermodynamic and kinetic studies, as well as number of Mn, Fe, Ni and Zn complexes that mimic functions of some enzymes or activate above mentioned small molecules and their cross-talk.

EPR Characterization of Heavy Main Group Radicals

George Cutsail III¹

¹Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany

The exploration of heavy main-group radicals is rapidly expanding, for which electron paramagnetic resonance (EPR) spectroscopic characterization plays a key role. EPR spectroscopy has the capacity to deliver information of the radical's electronic, geometric and bonding structure. I will present recent applications of EPR spectroscopy to As, Sb, and Bi centered radicals and the use of multifrequency EPR to resolve these complicated spectra. Additionally, I will introduce the application of parallel-mode EPR spectroscopy to aid in the complete analysis of bismuth radicals with extremely large hyperfine interactions.

POSTER PRESENTATIONS
(PP)

THz-EPR on light-induced high-spin states in main group compounds with an extension to frozen solutions

T. Al Said^a, K. Holldack^b, M. Neben^c, S. Schneider^c, A. Schnegg^d

^a Department Spins in Energy Conversion and Quantum Information Science, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 12489 Berlin, Germany

^b Department Optics and Beamlines, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 12489 Berlin, Germany

^c Institute of Inorganic Chemistry, Georg-August-Universität Göttingen, 37077 Göttingen, Germany

^d Max Planck Institute for Chemical Energy Conversion, 45470 Mülheim an der Ruhr, Germany

Field-domain Fourier-transform THz electron paramagnetic resonance (FD-FT THz-EPR) spectroscopy is a broadband high frequency / high magnetic field EPR technique, which is optimally suited for detecting large zero-field splittings (ZFS) up to hundreds of cm^{-1} and for studying strongly exchanged coupled systems [1]. This renders the method in particular useful to characterize the electronic structure of catalytically relevant high-spin ($S > 1/2$) transition metal complexes [2] and main group compounds [3]. A large group of these compounds, like photocatalysts [4] or photo-switchable molecules [5] must be studied under light irradiation to gain maximal insight in electronic structure – function relationships. However, this entails some experimental challenges, as the photogenerated states may be short-lived or created in a too low yield.

Here, we describe the experimental setup for light-induced THz-EPR measurements at the THz endstation of BESSY II, followed by the results of an FD-FT THz-EPR study on light-generated pnictinidenes (MPn , $S=1$) that serve as intermediates in chemical catalysis and synthesis [3]. The experimentally determined ZFS parameters from this sample series derived by systematic permutation of the metal ($M = \text{Pd}, \text{Pt}$) and the coordinating pnictogen ($\text{Pn} = \text{N}, \text{P}, \text{As}$) demonstrate the influence of spin-orbit coupling and can serve to benchmark relativistic effects in quantum-chemical methods. Finally, a methodical protocol for the extension to frozen solution experiments is outlined. Choices of solvents and detection limits are discussed using myoglobin as a model sample [6].

References:

- [1] Nehr Korn, J. *et al.*, J. Magn. Reson. **280** (2017) 10 – 19.
- [2] Krzystek J *et al.*, Inorg. Chem. **59** (2020) 1075 – 1090.
- [3] Schmidt-Räntsch, T. *et al.*, Angew. Chem. Int. Ed. **61** (2022) e202115626.
- [4] Prier, C. K., Rankic, D. A., MacMillan, D. W. C., Chem. Rev. **113** (2013) 5322-5363.
- [5] Dorel, R., Feringa, B. L., Chem. Commun. **55** (2019) 6477-6486.
- [6] Nehr Korn, J. *et al.*, Mol. Phys. **111** (2013) 2696 – 2707.

A versatile setup for FTIR spectroscopy in high magnetic fields

J. Dubnická Midlíková¹, M. Šedivý¹, A. Sojka², V. Tadeu Santana¹, Adam Dubroka^{1,3}, Petr Neugebauer¹

1. CEITEC—Central European Institute of Technology, Brno University of Technology, Purkyňova 123, 61200 Brno, Czech Republic

2. ITST - Institute of Terahertz Science and Technology, University of California, Santa Barbara, CA 93106-4170

3. Masaryk University, Faculty of Science, Kotlářská 267/2, 61137 Brno, Czech Republic

Fourier-transform infrared (FTIR) spectroscopy in high magnetic fields or simply FTIR magneto-spectroscopy is a powerful spectroscopic technique used to investigate many important effects in materials, e.g., electron spin resonance, cyclotron resonance, and transitions between Landau levels. Despite their enormous potential in solid-state physics, infrared magneto-spectrometers are still relatively rare. We present a versatile FTIR magneto-spectroscopic setup operating in the range of 5 – 10,000 cm⁻¹, high magnetic field up to 16 T and temperatures between 2-320 K. This setup allows us to perform a variety of magneto-optical measurements spanning the range from THz/far-infrared (FIR) to near-infrared (NIR). It consists of a commercial FTIR spectrometer coupled to a 16 T cryogen-free superconductive magnet by the custom-designed optical coupling and transmission probes designed for experiments with various detectors and samples in Faraday geometry. The functionality of the FTIR magneto-spectroscopic setup is demonstrated by the magneto-optical measurements on a cobalt-based single-molecule magnet (SMMs) in the FIR region and germanium in the NIR region. For the investigation of SMMs, spectroscopic techniques, such as EPR spectroscopy, are essential due to their ability to probe molecular and electronic properties directly. However, because of systems with large zero-field splitting, FTIR spectroscopy in the high magnetic field is needed to access fundamental transitions in SMMs. This setup¹ allows studying the EPR of SMMs with very large zero-field splitting, mainly based on transition metal complexes² or lanthanides³ that standard EPR systems cannot study since they do not provide experimental access to the magnetic resonance transitions. Besides, the FTIR magneto-spectroscopic setup can probe band structure and elucidate electronic properties of semiconductors, such as germanium, and novel 2D materials, such as graphene⁴.

1. Dubnická Midlíková et al., IEEE Trans. Inst. & Meas. 2023, *under review*.

2. J. Juráková et al., Inorganic Chemistry Frontiers 2022, 9.

3. R. Marx et al., Chemical Science 2014, 5, 8.

4. M. Orlita et al., Physical Review Letters 2008, 101, 267601.

International Workshop “EPR for Catalysis Research”

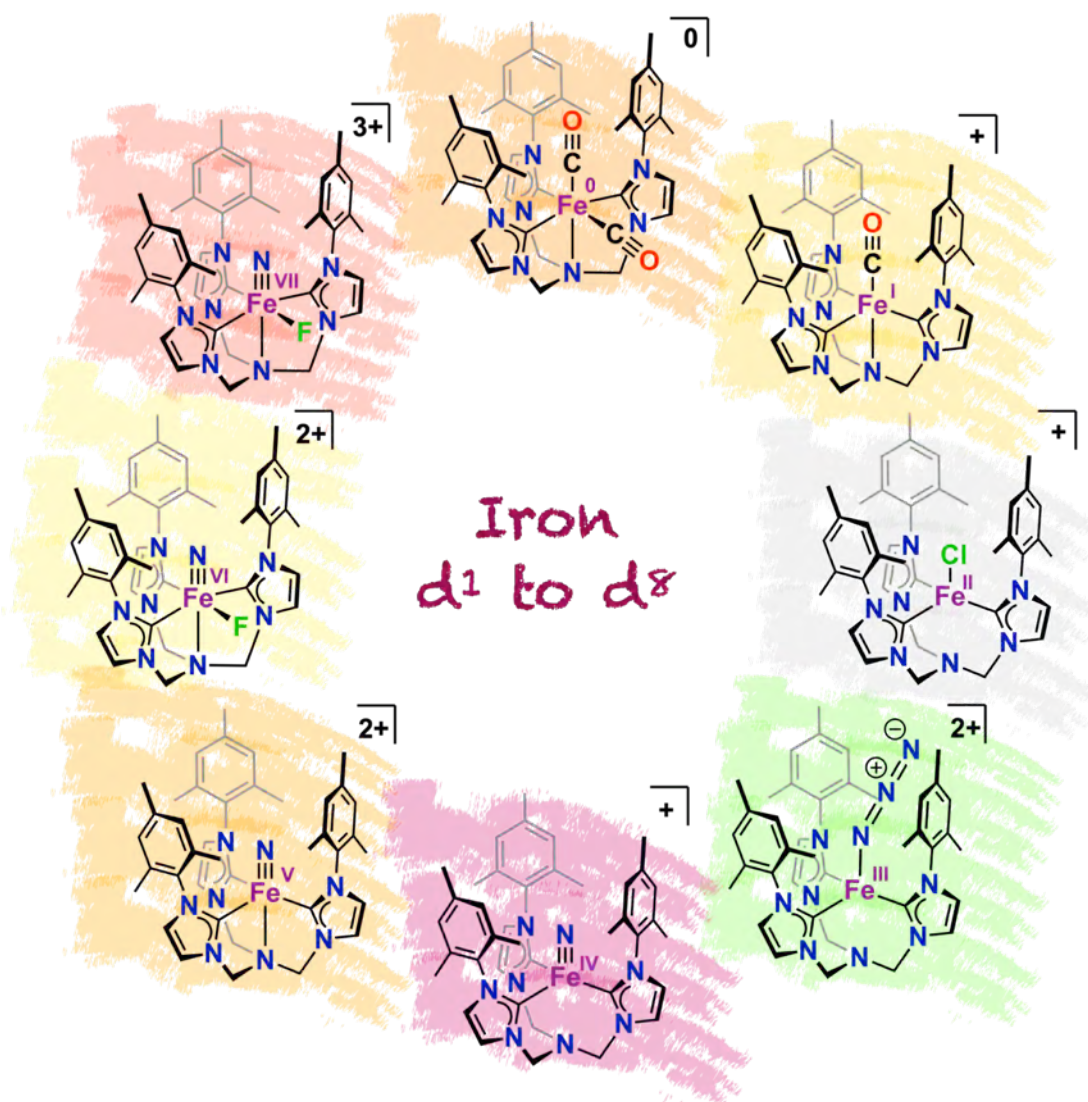
Iron in Eight Oxidation States

Lisa Gravogl^{*}, Martin Keilwerth, Frank W. Heinemann, and Karsten Meyer

Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Department of Chemistry and Pharmacy,
Inorganic Chemistry, Egerlandstraße 1, 91058 Erlangen, Germany

^{*}lisa.gravogl@fau.de

We show that the *tris*-carbene chelate *tris*-[2-(3-mesityl-imidazol-2-ylidene)methyl]amine (TIMMN^{Mes})^[1,2] is capable of supporting iron in oxidation states from 0 to 7+. While the [(TIMMN^{Mes})Fe] core structure remains intact over the entire series, the changes in the oxidation states are supported by the coordination of additional axial or equatorial co-ligands.



References

- [1] M. Keilwerth, L. Grunwald, W. Mao, F. W. Heinemann, J. Sutter, E. Bill, and K. Meyer, *J. Am. Chem. Soc.* **2021**, *143*, 1458-1465.
- [2] M. Keilwerth, W. Mao, S. A. V. Jannuzzi, L. Grunwald, F. W. Heinemann, A. Scheurer, J. Sutter, S. DeBeer, D. Munz, K. Meyer, *J. Am. Chem. Soc.* **2023**, *145*, 873-887.

***In situ* Continuous Wave Electron Paramagnetic Resonance Study of Dihydrogen Isotope-Selective Response on the Flexible Metal Organic Framework**

Muhammad Fernadi Lukman^{1*}, Sibor Chetry², Kavipriya Thangavel¹, Harald Krautscheid², Andreas Pöpl¹

¹ Felix Bloch Institute for Solid State Physics, University of Leipzig, Leipzig, Germany

² Universität Leipzig, Fakultät für Chemie und Mineralogie, Institut für Anorganische Chemie, Johannisallee 29, 04103 Leipzig, Germany

*muhammad_fernadi.lukman@uni-leipzig.de

Recently, the flexible MIL-53 (Al) metal organic framework (MOF) is reported to be a promising porous material which selectively respond to D₂ over H₂ by providing a secondary breathing mechanism ¹. In terms of detection scenario, there are only few spectroscopic techniques that can monitor this phenomenon including *in-situ* neutron powder diffraction (NPD) ^{1,2}. Alternatively, our current work put the emphasis on the utilisation of *in-situ* continuous wave electron paramagnetic resonance (CW-EPR) as a powerful characterization technique for adsorption of dihydrogen isotopes by deploying Cr³⁺ and VO²⁺ spin probes that are doped into the framework of MIL-53 (Al) MOF. Their zero-field splitting (Figure 1) and hyperfine coupling parameters are very sensitive to the local structure changes around Cr³⁺ (S = 3/2) and VO²⁺ (S = 1/2) with respect to H₂/D₂ adsorption-desorption process.

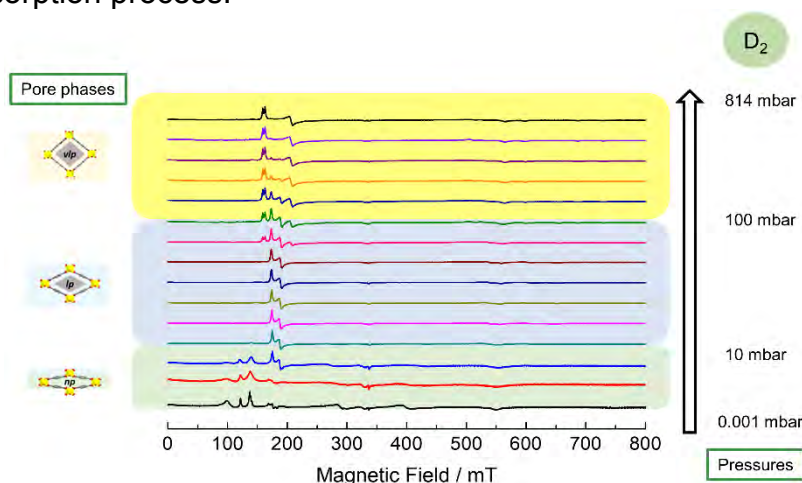


Figure 1: Pressure dependent of D₂ adsorption on Cr³⁺ doped (1 wt%) MIL-53 (Al) recorded by *in situ* CW-EPR at 23 K. Different colour shades represents various pore states: narrow pore (light blue), large pore (dark blue) and very large pore (light yellow) phases.

References:

- (1) Kim, J. Y.; Park, J.; Ha, J.; Jung, M.; Wallacher, D.; Franz, A.; Balderas-Xicohtencatl, R.; Hirscher, M.; Kang, S. G.; Park, J. T.; Oh, I. H.; Moon, H. R.; Oh, H. *J. Am. Chem. Soc.* **2020**, *142* (31), 13278–13282.
- (2) Bondorf, L.; Fiorio, J. L.; Bon, V.; Zhang, L.; Maliuta, M.; Ehrling, S.; Senkovska, I.; Evans, J. D.; Joswig, J.-O.; Kaskel, S.; Heine, T.; Hirscher, M. *Sci. Adv.* **2022**, *8* (15), 7035.

Rapid scan ESR: A Versatile Tool for the Spin Relaxation Studies at (sub)THz Frequencies

O. Laguta¹, M. Sedivy¹, V.T. Santana¹, A. Sojka^{1,2}, A. Marko¹, P. Neugebauer¹

1. CEITEC—Central European Institute of Technology, Brno University of Technology, Purkyňova 123, 61200 Brno, Czech Republic

2. present address: ITST - Institute of Terahertz Science and Technology, University of California, Santa Barbara, CA 93106-4170

The development of pulse electron spin resonance spectroscopy at microwave frequencies above 100 GHz is rather challenging and expensive task due to the low output power of modern high-frequency solid-state electronics. However, there is a number of scientific problems, e.g., DNP enhancement of NMR, that require spin relaxation measurements at THz frequencies. The rapid scan ESR is an alternative technique that does not require high microwave power and still provides information on the spin relaxation times. The method takes advantage of fast sweeps of the excitation microwave frequency over the ESR line. When the frequency sweep reaches a sufficiently high rate, distinct oscillations (also called wiggles) appear in the spectrum¹⁻³. It is possible to retrieve the undistorted (slow-scan) spectrum by employing the Fourier Transform analysis as Josef Dadok had demonstrated in NMR⁴. On the other hand, these oscillations bear information about the electron spin-spin relaxation time, which can be extracted via fitting the rapid scan spectrum using the modified Bloch equations. This technique allows one to capture the spin-spin relaxation time at the nanosecond time scale. Furthermore, the particular design of modern high-frequency ESR spectrometers greatly facilitates the multifrequency operation bringing the spin relaxation measurements to an unprecedentedly broad range of magnetic fields using only one ESR spectrometer (Fig. 1). Finally, we will discuss the future steps necessary to make the THz rapid scan ESR a convenient and easy to use tool for the broad scientific community.

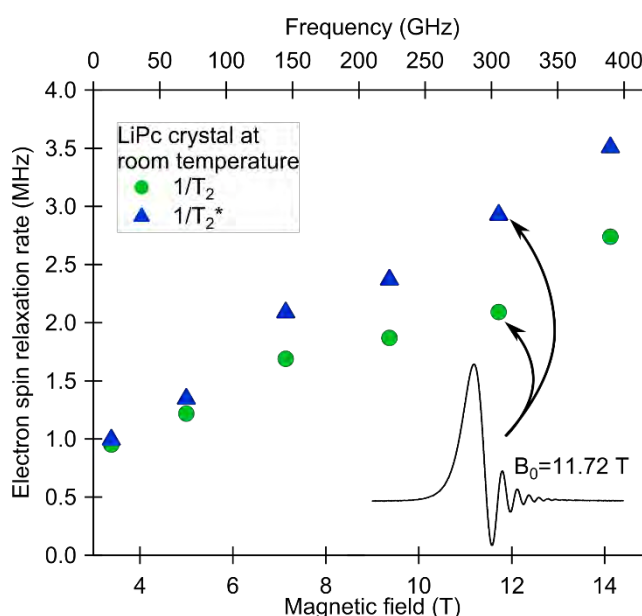


Fig.1 Magnetic field dependence of the electron spin relaxation times T_2 and T_2^ in LiPc at room temperature.*

1. J. W. Stoner et al., Journal of Magnetic Resonance 2004, 170, 127.
2. O. Laguta, M. Tuček, J. van Slageren and P. Neugebauer, Journal of Magnetic Resonance 2018, 296, 138.
3. O. Laguta, A. Sojka, A. Marko and P. Neugebauer, Applied Physics Letters 2022, 120, 120502.
4. J. Dadok and R. F. Sprecher, Journal of Magnetic Resonance (1969), 1974, 13, 243.

Solid-state NMR investigations on organic mechanochemical reactions

I.D.A. Silva^a, E. Bartalucci^a, C. Schumacher^b, L. Hendrickx^c, F. Puccetti^b, C. Quaranta^b, R. Dervişoğlu^a, R. Puttreddy^{b,d}, C. Bolm^b, T. Wiegand^{a,c}

igor.danciaes-almeida-silva@cec.mpg.de

^a Max Planck Institute for Chemical Energy Conversion, Mülheim/Ruhr, Germany

^b Institute of Organic Chemistry, RWTH Aachen University, Aachen, Germany

^c Institute of Technical and Macromolecular Chemistry, RWTH-Aachen University, Aachen, Germany

^d Department of Chemistry, University of Jyväskylä, Jyväskylä, Finland

The field of mechanochemistry has experienced impressive advances in the past years, which are reflected in versatile chemical and biological applications [1]. Pressure, for instance applied in ball-milling devices, is one of the most often reported energy inputs in mechanochemistry and a deeper mechanistic understanding of mechanochemically-induced reactions is fundamental to explore the whole potential for instance in organic synthesis. We herein used magic-angle spinning (MAS) solid-state NMR to investigate an aromatic bromination of a sufoximine (2-methyl-3*H*-2λ⁴-benzo[*c*]isothiazole 2-oxide) with *N*-bromosuccinimide (NBS) in a mixer ball mill. This approach allows the characterization of ball-milling products without introducing any further post-processing on the sample of interest. Further, mixing the solid educts in the NMR rotor enabled in-situ insights into the reaction. However, the centrifugal pressure induced in the rotor by MAS was not sufficient to lead to full conversion and unwanted side-reactions occurred. Apparently, on top of centrifugal forces, an efficient mixing of the starting materials was required for complete turnover[2]. We also present our first data on the mechanochemical formation of racemic associates of trifluoromethyl lactic acid, serine, and alanine formed by grinding crystals of the enantiopure compounds. Time-resolved solid-state NMR is also established as a tool to follow the self-disproportionation of scalemic mixtures of (*rac*) and (*S*) trifluoromethyl lactic acid[3].

[1] T. Frišćić, C. Mottillo, H. M. Titi, *Angew. Chem. Int. Ed.* **2020**, 59, 1018-1029

[2] E. Bartalucci et al. *Chem. Eur. J.* **2023**, e202203466

[3] V. A. Soloshonok et al. *J. Am. Chem. Soc.* **2007**, 129, 12112-12113

Octaazamacrocyclic Nickel(II) Complexes - Catalysts in Nylon Production Chain

M. Zalibera^{1*}, A. Dobrov², D. Darvasiová¹, L. Bučinský¹, I. Puškárová¹, P. Rapta¹, L. M. D. R. S. Martins³, A. J. L. Pombeiro³, and V. B. Arion²

¹ Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37 Bratislava, Slovak Republic

² Institute of Inorganic Chemistry, University of Vienna, Währinger Strasse 42, A-1090 Vienna, Austria

³ Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

* corresponding author: e-mail: michal.zalibera@stuba.sk

Keywords: redox non-innocent ligands, EPR, Nylon, spectroelectrochemistry

Abstract

Cyclohexanol, cyclohexanone, and their mixture (i.e., A/K oil) represent important precursors in the industrial production of nylon. The effective and selective oxidation of cyclohexane to the A/K oil can reduce both production costs and waste material generation. Transition-metal catalysts able to steer the reaction in the required direction are thus in high demand in the fiber industry.

A series of nickel(II) complexes with 15-membered and 14-membered octaazamacrocyclic ligands, as well as several diastereomeric dimers, were prepared in our lab. Their electrochemical behavior was investigated in detail, and the electronic structure of 1e-oxidized and 1e- reduced species was studied by EPR, UV-vis-near-IR spectroelectrochemistry, and density functional theory calculations indicating redox non-innocent behavior of the ligands. The compounds were tested in microwave-assisted solvent-free oxidation of cyclohexane by tert-butyl hydroperoxide to produce the industrially significant mixture of cyclohexanol and cyclohexanone (i.e., A/K oil). The catalytic results and the structure-activity relations obtained will be discussed.

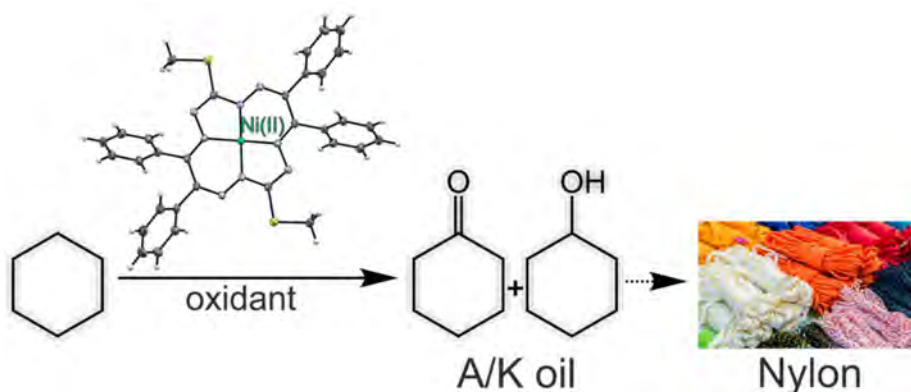


Figure 1. The scheme of catalytic conversion of cyclohexane to A/K oil

This project was supported by the Science and Technology Assistance Agency (contracts APVV-19-024, APVV-20-0213 and DS-FR-19-0035) and VEGA (contracts 1/0078/21 and 1/0504/20)

References

- [1] A. Dobrov et al., *Inorg. Chem.* 58 (2019) 11133–11145.
- [2] D. Darvasiova et al., *Electrochim. Acta* 326 (2019) 135006.
- [3] A. Dobrov et al., *Dalton Trans.* 51 (2022) 5151-5167.

EPR in Bio-Inorganic Chemistry: Detection of the Intermediates Involved in the Activation of Oxygen Species

Andrea Squarcina,^a Dominik Fehn,^b Derya Demirbas,^c Maurice van Gastel,^c and Ivana Ivanović-Burmazović^a

^a Department of Chemistry, Ludwig-Maximilian-Universität München, 81375 München, Germany.

^b Department of Chemistry and Pharmacy, FAU, 91058 Erlangen, Germany.

^c Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelmplatz 1, 45470 Mülheim an der Ruhr, Germany.

Email: andrea.squarcina@cup.uni-muenchen.de

In nature any failure in the mechanism of O₂ reduction turns out into the release of toxic reactive oxygen species (ROS).^[1] The natural defence against ROS is provided by the combined action of superoxide dismutases (SOD), catalases (CAT) and glutathione peroxidase that with a cascade mechanism convert the superoxide radical anion (O₂^{•-}) and H₂O₂ into O₂ and H₂O. On the other hand, the discovery and characterization of highly reactive oxo and superoxo intermediates in the catalytic cycles of several dioxygen activating enzymes has aroused the interests of many scientists to design bioinspired nonheme complexes which reactivity and features should mime the one of the enzymatic reactive species.^[2] Here we discuss some mono and dinuclear Me-O₂ intermediates, recently first reported by us, involved in the oxidation of organic substrates and in the scavenging of ROS respectively.^[3,4]

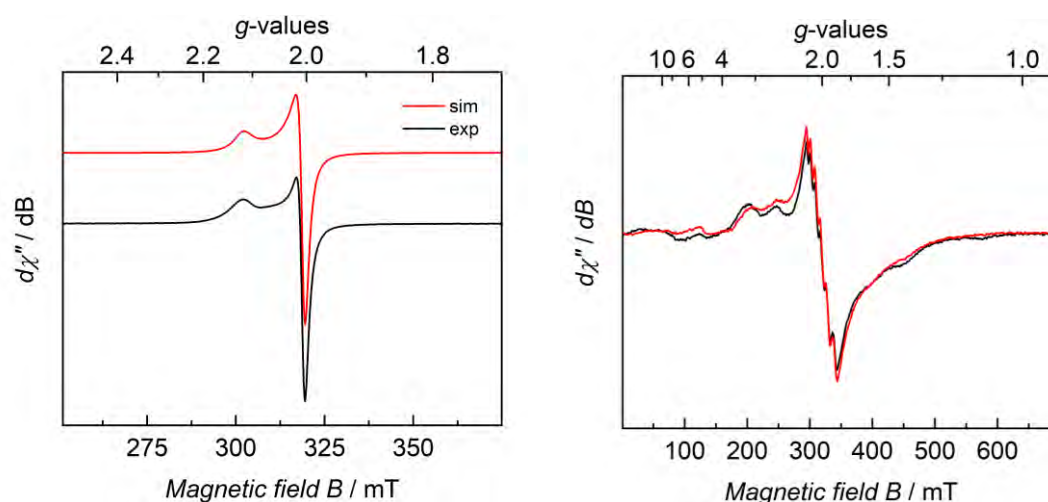


Figure 1. EPR spectra of the key Me-O₂ intermediates involved in oxygen activation.

References:

- [1] Finkel, T.; Holbrook, N. J. *Nature*, **2000**, 408, 239.
- [2] Sahu, S.; Goldberg, D. P. *J. Am. Chem. Soc.* **2016**, 138, 11410–11428
- [3] Squarcina, A.; Fehn, D.; Senft, L.; Langer, J.; Ivanović-Burmazović, I. *Z. Anorg. Allg. Chem.* **2021**, 809–814.
- [4] Squarcina, A.; Fehn, D.; Scheitler, A.; Senft, L.; Franke, A.; Zahl, A.; Puchta, R.; Meyer, K.; Ivanović-Burmazović, I. *ACS Catal.* **2023**, just accepted.

An EPR/ENDOR investigation of a Mn_2O_2 intermediate model for class Ib RNRs

Amanda Opis Basilio^{1*}, Beatrice Battistella¹, Kallol Ray¹, Thomas Lohmiller^{1,2}

¹Institut für Chemie, Humboldt-Universität zu Berlin, Berlin, Germany

²EPR4Energy Joint Lab, Department SE-ASPIN, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany

*amanda.opis.basilio@hu-berlin.de

The high valent $\text{Mn}^{\text{III}}-(\mu\text{-oxo})_2\text{-Mn}^{\text{IV}}$ species formed in the activation of superoxide ($\text{O}_2^{\cdot-}$) in the dimanganese(II) active sites of class Ib ribonucleotide reductases (RNRs) is responsible for the formation of a stable tyrosyl radical intermediate, storing the oxidizing equivalent for subsequent enzymatic transformation.

The synthesis of diamanganese model complexes that can perform such reactions are the aim of biomimetic approaches. Recently, the synthesis, characterization, and reactivity of a new binuclear Mn_2 complex were reported by our group.[1] The results from two different spectroscopic techniques, however, showed some ambiguity, suggesting different Mn oxidation states and O_2 -binding modes in the intermediate. While resonance Raman (rRaman) shows the presence of a $\text{Mn}^{\text{II}}-(\mu\text{-peroxo})\text{-Mn}^{\text{III}}$ motif (Figure 1b), its $g=2$ CW-EPR signal (Figure 1c, present besides a smaller $g\approx 4$ signal) exhibits the characteristic shape and hyperfine constants of $\text{Mn}^{\text{III}}-(\mu\text{-oxo})_2\text{-Mn}^{\text{IV}}$ species, such as the $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$ intermediate of the enzyme co-factor.

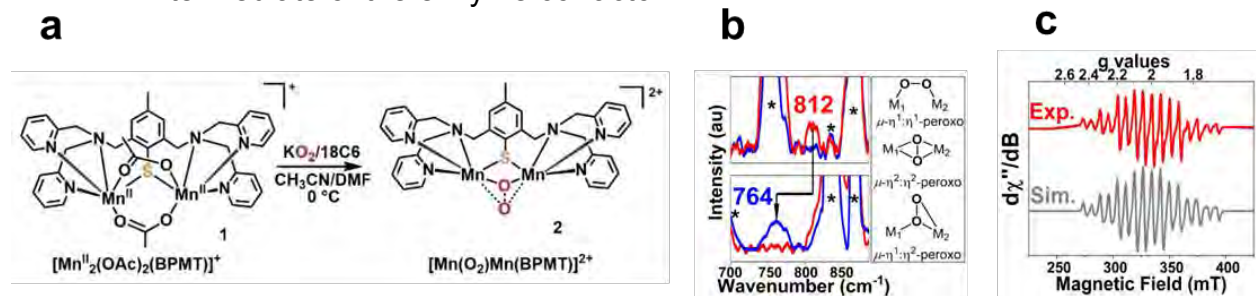


Figure 1: a) Reaction of $[\text{Mn}^{\text{II}}_2(\text{OAc})_2(\text{BPMT})](\text{ClO}_4)$ $\text{O}_2^{\cdot-}$ to form intermediate 2. b) rRaman spectra and c) experimental and simulated CW-EPR spectra of intermediate 2.[1]

This study aims to investigate the binding mode for such intermediates in greater detail, using different EPR techniques, such as parallel-mode and pulse EPR (Rabi nutations, ^{55}Mn Electron Nuclear Double Resonance (ENDOR)), to understand the Mn oxidation states associated with both the $g=2$ and $g\approx 4$ signals and if the system forms only one or two isolable intermediates upon oxidation.

Our findings will contribute to a better understanding of the catalytic mechanism of class Ib RNRs and the role of key intermediates from the model for this enzyme.

References:

[1] B. Battistella et al., *Angew. Chem. Int. Ed.* **2023**, 62, e202217076

Nanotubide Electrodes for in-situ film-electrochemical EPR Investigations of Radicals in (Electro)catalysis

Yunfei Dang¹, Maryam Seif-Eddine¹, Alex Ford¹, Milo S. P. Shaffer¹, and Maxie M. Roessler¹

¹ Imperial College London, Department of Chemistry, Molecular Sciences Research Hub, 82 Wood Lane, London W12 0BZ, UK

y.dang20@imperial.ac.uk

The combination of film electrochemistry (FE) and electron paramagnetic resonance (EPR) spectroscopy, FE-EPR, has attracted attention owing to its ability to monitor the redox behaviour of paramagnetic centres within a molecule of interest during both catalytic and non-catalytic reactions. The proof-of-principle has been established using mesoporous indium tin oxide (meso-ITO) as working electrodes (WE), but they still have disadvantages, namely a limited potential and pH range, fragility, and intrinsic EPR signal.¹

To address these shortcomings, here, carbon nanotubes (CNTs) are used as an alternative. CNT buckypaper with high conductivity, high porosity and good robustness was made from reductively charged nanotubide solution,² and subsequently formed into electrodes. The optimised composition and geometry were determined and a typical nitroxide redox-spin label (a TEMPO derivative) was immobilised onto the buckypaper after electrochemical diazonium functionalisation. The FE-EPR CNT WE and the FE-EPR cell were designed and prepared (Fig. a), and the first example of in-situ FE-EPR measurements at room temperature was achieved using this set-up (Fig. b-d). Excellent consistency between the reduction potential of the nitroxide obtained from CV (0.812 V) and in-situ FE-EPR (0.806 V) demonstrated the compatibility of the CNT WE with FE-EPR and the direct, accurate potential control of this set-up. This work, therefore, not only demonstrates the feasibility of using CNT materials to extend the applications of FE-EPR beyond those possible with ITO, but also reveals its potential to investigate the mechanism of TEMPO catalysed alcohol oxidation.

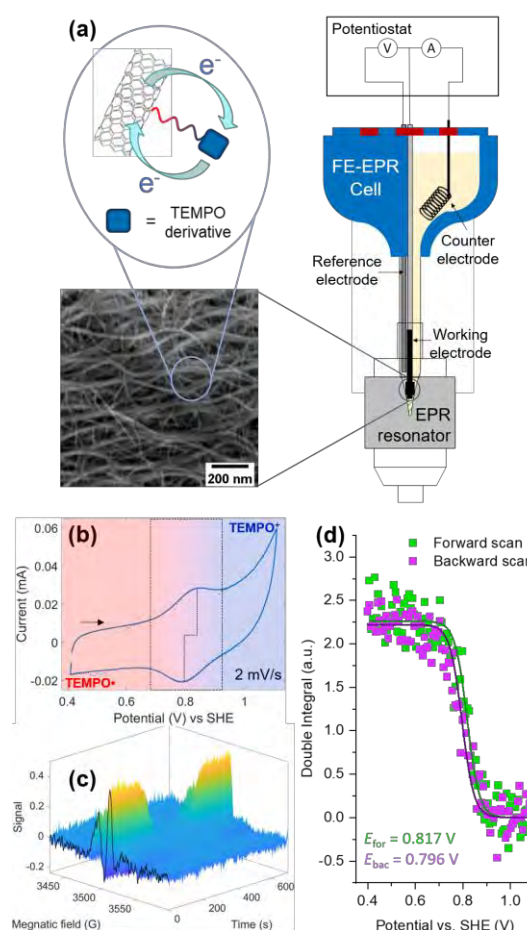


Fig: (a) Schematic of the in-situ FE-EPR set-up; (b&c) real-time CV-EPR measurement; (d) Nernst fitting curves revealing the transition between EPR-active TEMPO radical to its EPR-silent oxoammonium species TEMPO⁺.

¹ K. Abdiaziz, E. Salvadori, K. P. Sokol, E. Reisner and M. M. Roessler, *Chem. Commun.*, 2019, **55**, 8840-8843.

² P. Sirisinudomkit, E. Senokos, N. Rubio and M. S. P. Shaffer, *Mater. Adv.*, 2021, **2**, 1981-1992.

Title: A submersible rapid scan EPR-on-a-chip (RS-EPRoC) dipstick sensor for dissolved oxygen detection

Authors: Joseph E. McPeak^{1,2}, Silvio Künstner^{1,3}, Anh Chu⁴, Martin Poncelet^{5,6}, Benoit Driesschaert^{5,6}, Jens Anders^{4,7}, and Klaus Lips^{1,8}

¹Berlin Joint EPR Laboratory and EPR4Energy, Department Spins in Energy Conversion and Quantum Information Science (ASPIN), Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany

²Novo Nordisk Foundation EPR Center, Department of Chemistry, University of Copenhagen, Copenhagen, Denmark

³EPR4Energy, Max-Planck-Institut für Chemische Energiekonversion, Mülheim an der Ruhr, Germany

⁴Institute of Smart Sensors, Universität Stuttgart, Stuttgart, Germany

⁵Department of Pharmaceutical Sciences, School of Pharmacy, West Virginia University, Morgantown, West Virginia, USA

⁶In Vivo Multifunctional Magnetic Resonance Center, Robert C. Byrd Health Sciences Center, West Virginia University, Morgantown, West Virginia, USA

⁷Center for Integrated Quantum Science and Technology (IQST), Stuttgart and Ulm, Germany

⁸Berlin Joint EPR Laboratory, Fachbereich Physik, Freie Universität Berlin, Berlin, Germany

Electron paramagnetic resonance (EPR) is an accurate and efficient technique to probe the environment of paramagnetic species in many applications across materials science, chemistry, and biology. Dynamic processes are routinely investigated using EPR; however, these applications are typically limited by the form factor of resonator-based EPR spectrometers such that either the entire process must be confined to the resonator with typical sample volumes of less than 1 cm³, or some sampling thereof must be considered in a stopped-flow fashion. The EPR-on-a-chip (EPRoC) device circumvents these limitations by integrating the entire EPR spectrometer into a single microchip thereby expanding the accessible sample environments for EPR measurements. We have recently developed an EPRoC device that may be submerged in fluid solution to form a dipstick EPRoC sensor. In this approach, the coil of a voltage-controlled oscillator with a diameter of a few hundred micrometers is used as the microwave source and detector simultaneously, operating under a protective coating such that the device may be placed in the sample solution directly. Additionally, improvements in sensitivity via rapid scan EPR have been recently demonstrated to enhance the capabilities of the EPRoC, thereby increasing the accessible applications where SNR per measurement time is the fundamental limit [1]. To improve upon the capabilities of the RS-EPRoC platform, a frequency-swept frequency modulated detection scheme has been implemented to allow fast scan rates over wide sweep ranges. The herein reported device combines the practicality of a dipstick EPRoC sensor with the enhanced sensitivity of FM-rapid scan methods to allow detection of triarylmethyl (trityl) oxygen-sensitive probes dissolved in aqueous solutions [2]. The resolving ability of the sensor is demonstrated such that with careful calibration, the EPRoC may be employed to monitor dissolved oxygen in fluid solution in an online fashion, enabling the possibility to utilize the EPRoC dipstick sensor in applications where paramagnetic reporter molecules are required.

1. S. Künstner, A. Chu, K. P. Dinse, A. Schnegg, J. E. McPeak, B. Naydenov, J. Anders, and K. Lips, *Mag. Res.*, 2, 2, 673-687, **2021**
2. U. Sanzhaeva, M. Poncelet, O. Tseytlin, M. Tseytlin, M. Gencheva, T. D. Eubank, V. V. Khramtsov, and B. Driesschaert, *J. Org. Chem.*, 85, 10388-10398, **2020**

EPR on a Chip for Spectro Electrochemistry

Takuma Sato, Silvio Künstner, Kaltum Abdiaziz, Alexander Schnegg
Max Planck Institute for Chemical Energy Conversion, 45470 Mülheim an der Ruhr, Germany

In order to design the ideal catalyst, it is necessary to employ an operand/in-situ technique, which monitors and gains in-depth insights into how catalysis proceeds under its reaction. In response to this need, the spectrochemical EPR (SEC-EPR), which combines electrochemistry and electron paramagnetic resonance (EPR), has gained prominence in electrochemical catalysis.

This study proposes a new approach using the EPR on a chip (EPRoC) sensor [1]. Our proof-of-concept experiment for electrochemical redox reaction of methyl viologen [2] involves submerging the EPRoC sensor in a pseudo-electrochemical cell filled with an aqueous solution. The primary benefit of this method is the absence of mechanical limitations (a resonator), facilitating easy integration with other analytical tools, and expanding potential applications even to lossy solutions at ambient temperatures.

[1] A. Chu et al. 2018 ISSCC, San Francisco, CA, USA, 2018, 354.

[2] J. Ding et al. J. Mater. Chem. A, 2019,7, 23337.

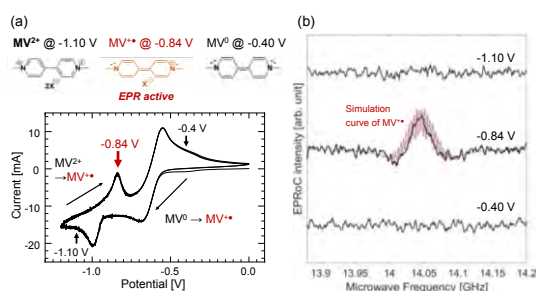


Figure. (a) The generated methyl viologen (MV) molecules (top) and cyclic voltammogram curve (bottom). (b) EPRoC spectra recorded at different potentials (black solid) and a simulated curve of $MV^{•+}$ (red dotted).

Magnetic Resonance Spectroscopy of Functional Materials: From Catalysts to Electroceramics

Pedro B. Groszewicz – p.groszewicz@tudelft.nl

Understanding the relation between properties and the structure at the local scale is a fundamental aspect required towards the development of functional materials. It will play an important role within the context of decarbonising the chemical/energy industry, in particular for materials which average structure cannot be easily assessed, or deviates from the local scale due to disorder or dynamics.

Magnetic resonance spectroscopic methods can offer an instrumental contribution in this regard, given their sensitivity to the local structure and their wide applicability across various material classes. Examples range from heterogeneous catalysts as a more sustainable means to produce chemical feedstock, electroceramic oxides required for high-power electronics, to ion conducting solids that may enable solid oxide cells as an efficient electrochemical reactor in a CO₂-neutral future.

In a first case, I will show how ³¹P chemical shift anisotropy can be used to explain differences in catalytic behaviour of Au nanoparticles (AuNP) stabilized by secondary phosphine oxide (SPO) ligands, and the marked effect of alkyl or aryl substituted SPOs on the selectivity towards hydrogenation of aldehyde moieties.[1]

A second example will cover lead-free alternatives to high-energy density dielectric oxides, and how the analysis of ²³Na electric field gradient and chemical shift helps one to understand the effect of chemical substitution in NaNbO₃ with Sr, Sn and Mn, as a means to stabilize a reversible antiferroelectric (AFE) state, advantageous for its use in high-power capacitors.[2,3]

Finally, a third point demonstrates how high-temperature ¹⁷O NMR can be used to assess dynamics of the local scale in La₂Mo₂O₉ (LAMOX), an oxide proposed as alternative solid-state electrolytes.[4]

[1] [*Journal of the American Chemical Society*, 137, 7718 \(2015\)](#)

[2] [*Chemistry of Materials*, 33, 266 \(2020\)](#)

[3] [*Nature Communications* 14, 1525 \(2023\)](#)

[4] *in preparation*

Using Hyperfine Spectroscopy to Map Out the Active Site of Lytic Polysaccharide Monooxygenases

Julia Haak^{1,2*}, Ole Golten³, Morten Sørli³, Vincent Eijsink³, George E. Cutsail III^{1,2}

¹Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany

²University of Duisburg-Essen, Essen, Germany

³Norwegian University of Life Sciences, Ås, Norway

*julia.haak@cec.mpg.de

Lytic polysaccharide monooxygenases (LPMOs) are monocopper enzymes, that catalyse the oxidative depolymerization of polysaccharides like cellulose or chitin. The active site of LPMOs is composed of the copper center, that is coordinated by one N-terminal histidine in bidentate fashion and an additional histidine side chain ('Histidine Brace'). [1] Electron Paramagnetic Resonance (EPR) Spectroscopy is the technique of choice to probe the Cu(II) center for its electronic and geometric properties, which are encoded in the **g**- and **A**-tensor. Albeit great information can be obtained from the hyperfine interaction **A**, it can often only be determined for large couplings, like ^{63/65}Cu or ¹⁴N couplings, from EPR spectra directly. To also observe smaller couplings, like ¹H hyperfine interactions, advanced EPR techniques, like ENDOR (Electron-Nuclear Double Resonance) can be employed.

While a variety of EPR studies for various LPMOs was reported and discussed, [2,3] Hyperfine Spectroscopy has rarely been employed. Herein, we report on ENDOR experiments of the well-studied chitin active LPMO SmAA10A, to determine hyperfine and nuclear quadrupole interactions of ¹H, ¹⁴N and ¹⁵N nuclei, allowing for a detailed structural interpretation of the active site.

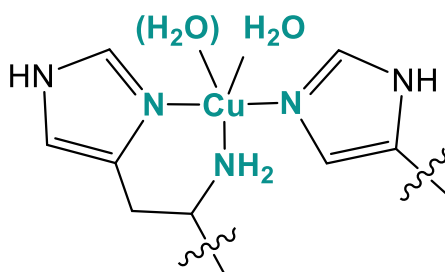


Figure 1: Copper Histidine Brace in LPMOs.

[1] Vaaje-Kolstad, G., Westereng, B., Horn, S. J., Liu, Z., Zhai, H., Sørli, M., Eijsink, V., G. H, *Science*, **2010**, 330, 219 – 222.

[2] Lindley, P. J., Parkin, A., Davies, G. J., Walton, P. H., *Faraday Discuss.*, **2022**, 234, 336 – 348.

[3] Gómez-Piñeiro, R. J., Drosou, M., Bertaina, S., Decroos, C., Simaan, A. J., Pantazis, D. A., Orio, M., *Inorg. Chem.*, **2022**, 61, 8022-8035.

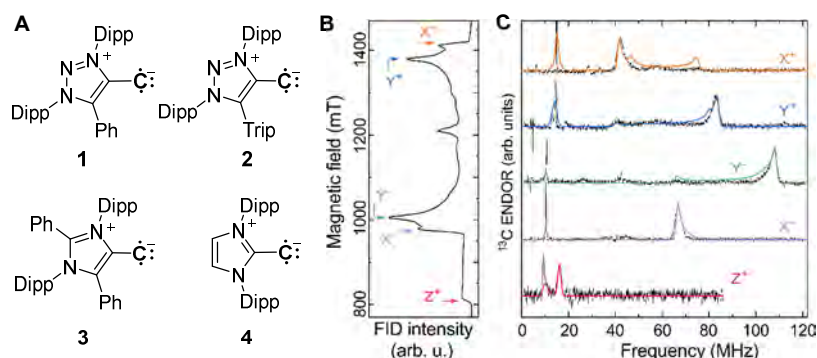
EPR/ENDOR Characterization of Triplet Vinylidenes

Y. Kutin¹, J. Reitz¹, P. W. Antoni¹, A. Savitsky¹, D. A. Pantazis², M. M. Hansmann¹, M. Kasanmascheff¹

¹ TU Dortmund University, Otto-Hahn-Str. 6, 44227 Dortmund, Germany

² MPI für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany

Vinylidenes are a class of compounds containing a monosubstituted carbon atom. Similar to carbenes, vinylidenes can possess a singlet or triplet ground state, the latter featuring two unpaired electrons on the terminal carbon. Singlet vinylidenes have been proposed as intermediates in a series of organic reactions, and very few were studied by matrix isolation or gas-phase spectroscopy. Triplet vinylidenes, however, had remained a theoretical prediction prior to our recent EPR/¹³C-ENDOR identification of the first ground-state triplet vinylidene [1]. The successful synthesis of stable diazoalkenes enabled the entry into this new fundamental compound class [2,3]. However, in contrast to the rich chemistry of triplet carbenes, triplet vinylidenes remain mostly unexplored. Here, we report the low-temperature isotope-sensitive EPR/ENDOR characterization of several members of this newly established carbon-centered diradical class. The vinylidenes were photochemically generated from a series of stable diazoalkenes featuring a five-membered heterocycle (Fig. A).



(A) Representative vinylidene structures investigated in this study. (B) Q-band EPR spectrum of **1** ($T = 6\text{ K}$). (C) ¹³C ENDOR spectra of **1** at canonical positions with simulations.

In our initial study, we demonstrated the triplet species formation upon UV irradiation of the precursor (Fig. B). However, the zfs parameter D was in the range typical for the well-known triplet carbenes. Key to recognizing the species as a vinylidene was the ¹³C hyperfine tensor of the terminal carbon, obtained from orientation-selective Davies ENDOR (Fig. C). A distinctly small A_{iso} value demonstrated that the compound's electronic structure was significantly different from that of carbenes, in excellent agreement with DFT calculations.

distinctly small A_{iso} value demonstrated that the compound's electronic structure was significantly different from that of carbenes, in excellent agreement with DFT calculations.

In this continued work, we characterize the electronic structure and thermal stability of several triplet vinylidenes featuring an imidazole or triazole backbone [1-3]. The class commonalities, effects of substituent groups and strategies for stability increase are investigated. The exploration of this compound class can reveal opportunities for exciting new applications.

References:

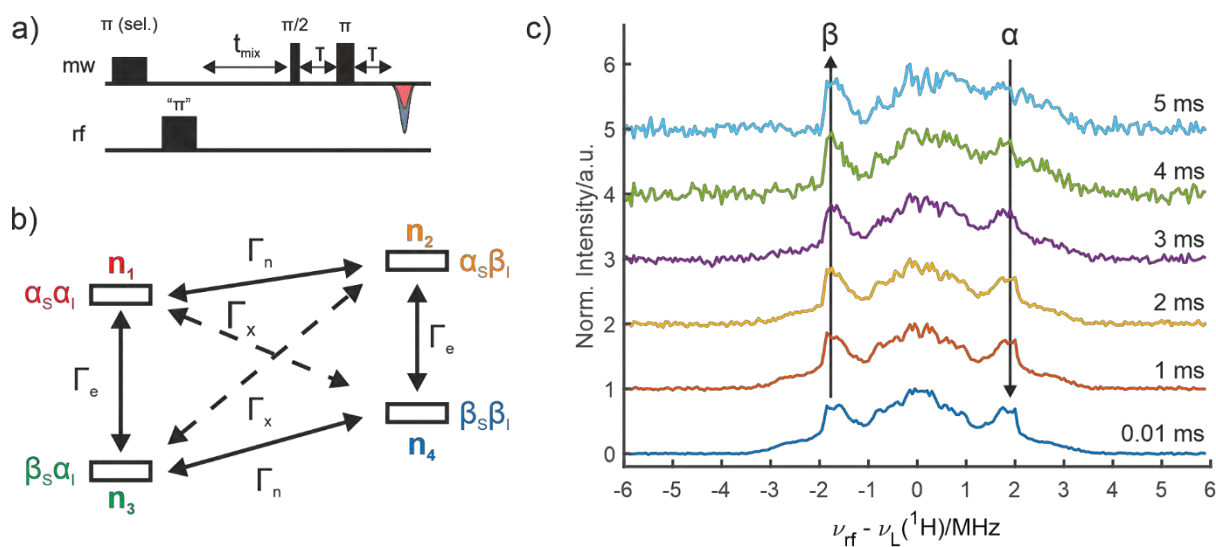
- [1] Kutin, Y. et al. *JACS* 2021, 143, 21410.
- [2] Antoni, P.W. et al. *Nat. Chem.* 2021, 13, 587.
- [3] Varava, P. et al. *Nat. Chem.* 2021, 13, 1055.

Relaxation Rates from Davies ENDOR variants for Ti(III) model catalysts

Julian Stropp¹, Yuya Kakiuchi¹, Sergei Kuzin¹, Christophe Copéret¹ and Daniel Klose¹

¹ Department of Chemistry and Applied Biosciences, ETH Zürich, 8093 Zürich, Switzerland

Ti(III) complexes are commonly used in homo- and heterogeneous catalysis such as Ziegler-Natta polymerization. Structural information from magnetic interactions quantified by the spin Hamiltonian parameters can be obtained by probing the paramagnetic active sites with EPR spectroscopy. This helps to elucidate mechanisms of such catalytic reactions. [1] In this project, we characterize Ti(III) model catalysts with Davies Electron Nuclear Double Resonance (ENDOR) spectroscopy. Beyond the determination of hyperfine and nuclear quadrupolar interactions of nuclear spins in the vicinity of a paramagnetic metal center, we focus on the measurement of relaxation rates of those spins, since they harbour information on electronic structure that is currently largely inaccessible and hence unused. At low temperatures (< 20 K) and sufficient magnetic fields (Q-band and higher) line asymmetries may appear in the Davies ENDOR spectrum (Fig. c) which depend on the electron, nuclear and cross relaxation rates (Fig. b) as well as on the mixing time, the shot repetition time, and the sign of the hyperfine coupling. [2] We assess the performance of the previously reported ENDOR variants Variable Mixing Time (VMT) ENDOR and Saturation Pulsed (SP) ENDOR for disentangling the different relaxation rates in titanium model systems, including for low-gamma nuclei, and identify the current limits of the techniques. [2,3] In doing so, we move a step closer towards determining nuclear spin relaxation times for nuclei close to paramagnetic metal centers.



a) Variable Mixing Time ENDOR pulse sequence b) Relaxation pathways of an idealized two-spin system c) Proton VMT ENDOR spectra of a Ti(III) catalyst at several mixing times

[1] Ashuiev, A., et al., J. Am. Chem. Soc. 2021, 143, 26, 9791–9797

[2] Morton, J. et al., J. of Magn. Res. 2008, 191, 2, 315–321

[3] Epel, B., et al., J. of Magn. Res. 2001, 148, 2, 388–397

Short-Range Electronic Interactions between Vanadium and Molybdenum in Bimetallic SAPO-5 Catalysts Revealed by Hyperfine Spectroscopy

Yu-Kai Liao,^{1,2} Valeria Lagostina,¹ Enrico Salvadori,¹ Martin Hartmann,³ Andreas Poepl,² Mario Chiesa¹

¹ Department of Chemistry and NIS Centre of Excellence, University of Turin, via Giuria 9, 10125 Torino, Italy.

² Felix Bloch Institute for Solid State Physics, Leipzig University, Linnéstr. 5, 04103 Leipzig, Germany

³ Erlangen Center for Interface Research and Catalysis (ECRC), FAU Erlangen-Nürnberg, Erlangen, Germany.

Structure-property correlations and mechanistic implications play an important role in the design of single-site catalysts for the activation of small molecules. [1, 2] Whereas the microporous silico-aluminophosphate (SAPO) is widely used for catalytic application due to its high surface area and unique porous structures, its catalytic activity can be further enhanced by engineering, redox-active site via simultaneous incorporation of two different transition-metal ions. [3]

In this work, we present the HYSCORE characterization of a vanadium-molybdenum bimetallic SAPO-5 catalyst, elucidating the localization of the two active metals, whilst simultaneously monitoring their redox behaviour. Molybdenum ions have been introduced in the porous structure starting from Mo(CO)₆ vapours, and subsequent oxidation with oxygen at 300°C. After this treatment, VCl₄ vapours were contacted with the solid sample leading to the Mo/V bimetallic catalyst.

CW-EPR showed the presence of Mo⁵⁺ and V⁴⁺ paramagnetic species, while hyperfine sublevel correlation spectroscopy (HYSCORE) spectra (Fig.1) provided evidence for the presence of V⁴⁺-O-Mo⁶⁺ linkages. The spin density transfer from the vanadium to the molybdenum is similar to the one observed for mixed valence V⁴⁺-O-V⁵⁺ dimer species [4] on oxide supports and calls for metal-metal synergy of relevance in catalytic reactions. [5]

With this work, we show a new method to prepare bimetallic SAPO-5 catalysts and the importance of EPR hyperfine spectroscopy in elucidating their geometric and electronic structure.

[1] Adams, A. H.; et al. *J. Mol. Catal. A: Chem.* **2004**, 216, 67-74

[2] Maurelli, S.; et al. *Chem. Commun.* **2012**, 48, 8700-8702

[3] Hartmann, M.; Kevan, L. *Chem. Rev.* **1999**, 99, 635-664

[4] Lagostina, V.; et al. *J. Catal.* **2022**, 406, 28-38

[5] Leithal, R. M.; et al. *J. Am. Chem. Soc.* **2013**, 135, 8, 2915–2918

Acknowledgements: This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 813209